

Nov. 9, 1954

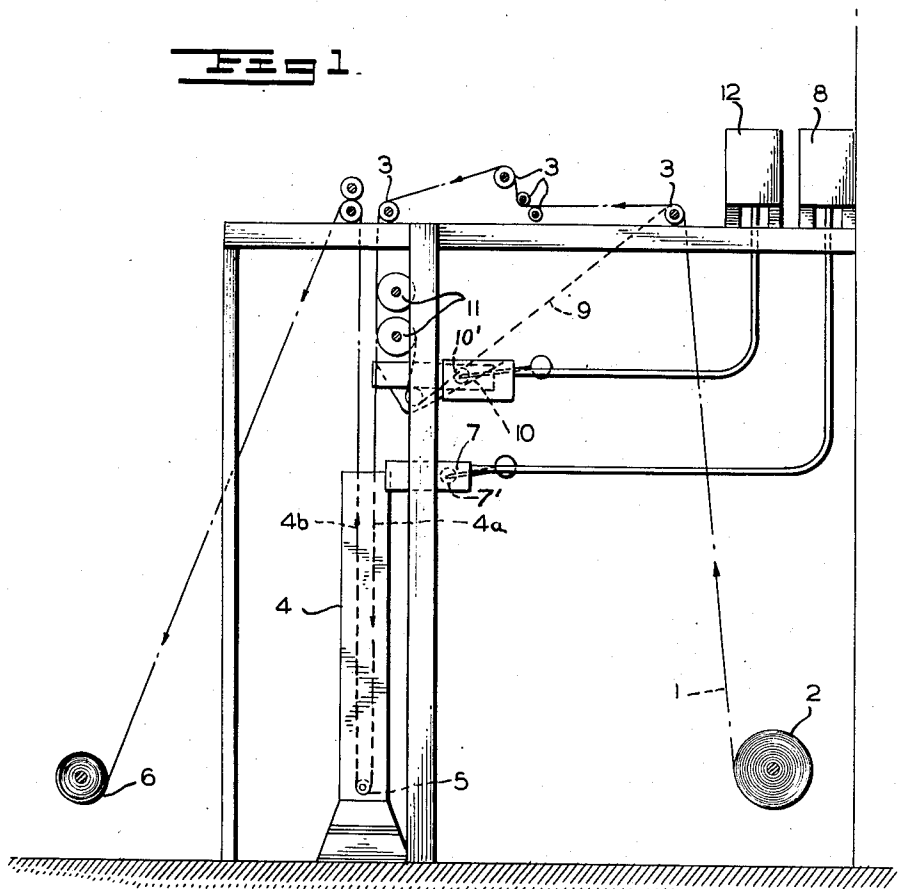
R. S. E. HANNAY ET AL

2,693,995

PROCESS AND APPARATUS FOR DYEING OR PERFORMING RELATED
PROCESSES UPON TEXTILES USING MOLTEN METAL

Filed Feb. 3, 1954

5 Sheets-Sheet 1



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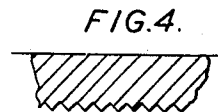
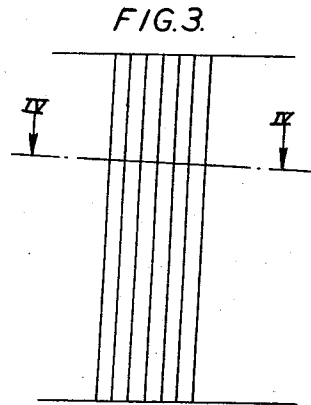
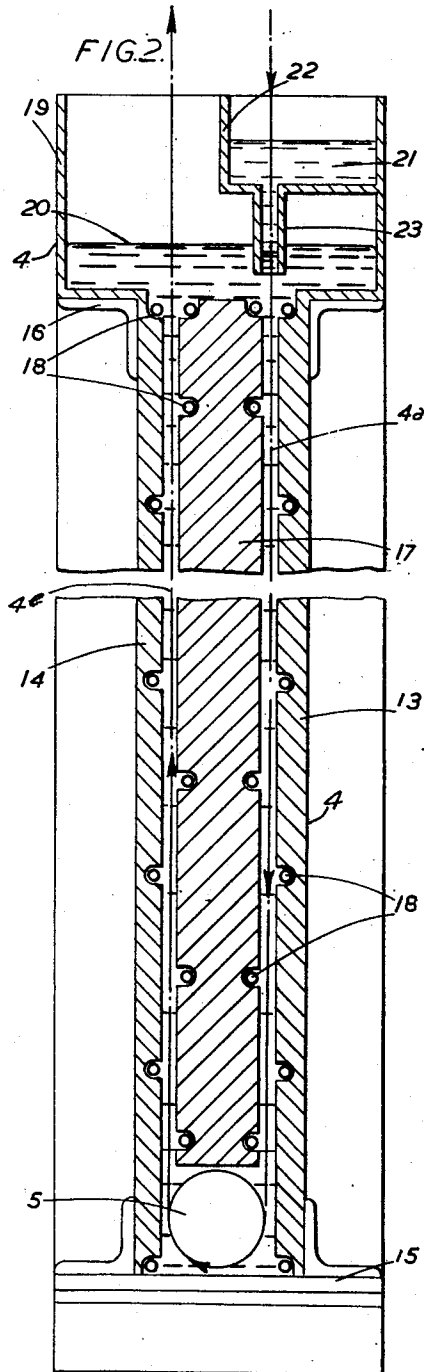
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5 Sheets-Sheet 2



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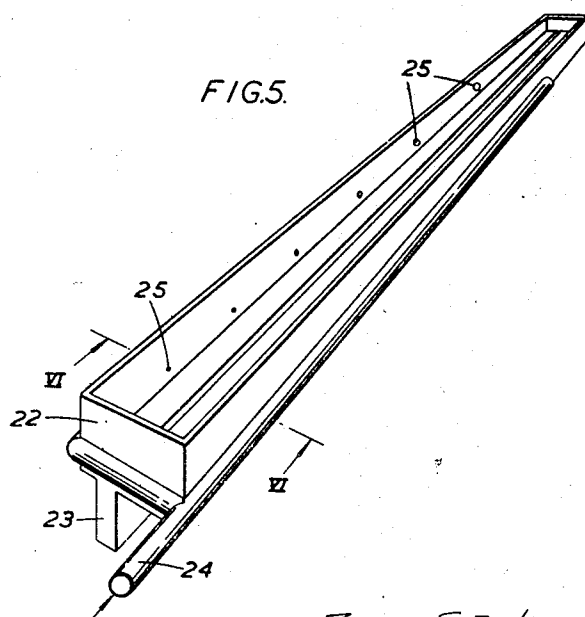
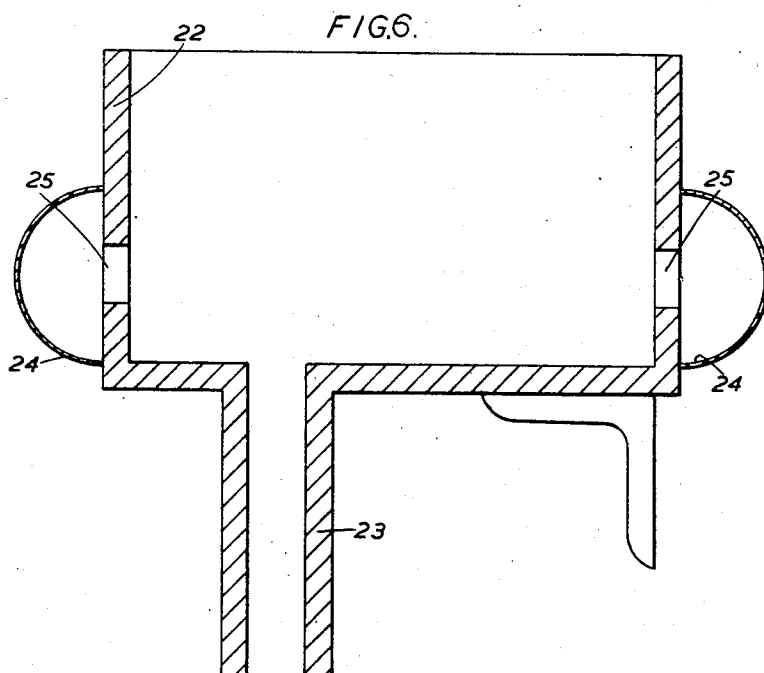
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Filed Feb. 3, 1954

5 Sheets-Sheet 3



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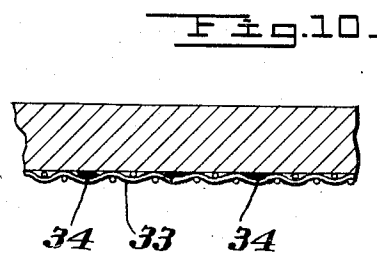
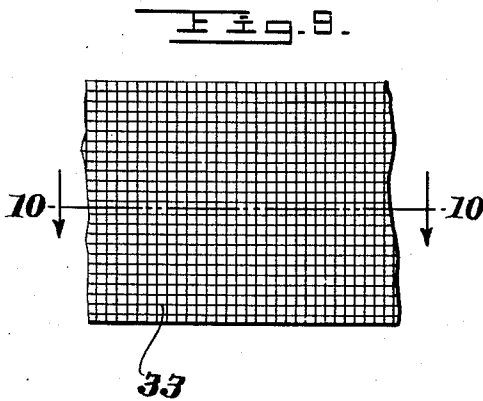
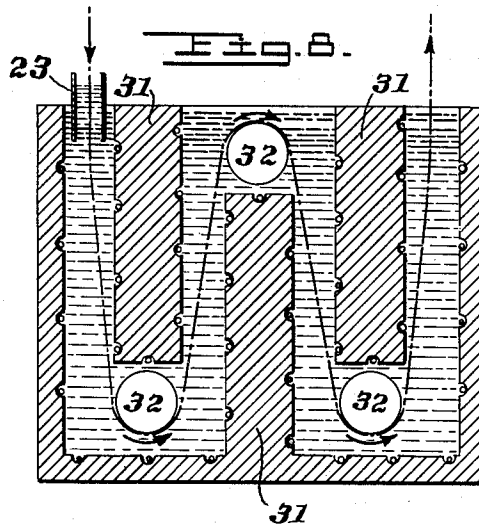
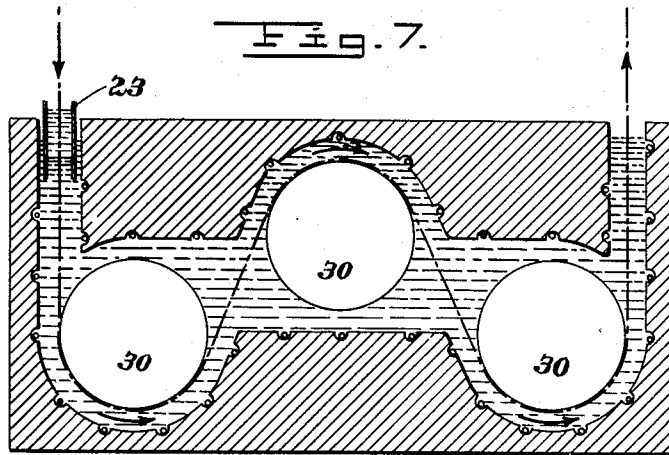
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Filed Feb. 3, 1954

5 Sheets-Sheet 4



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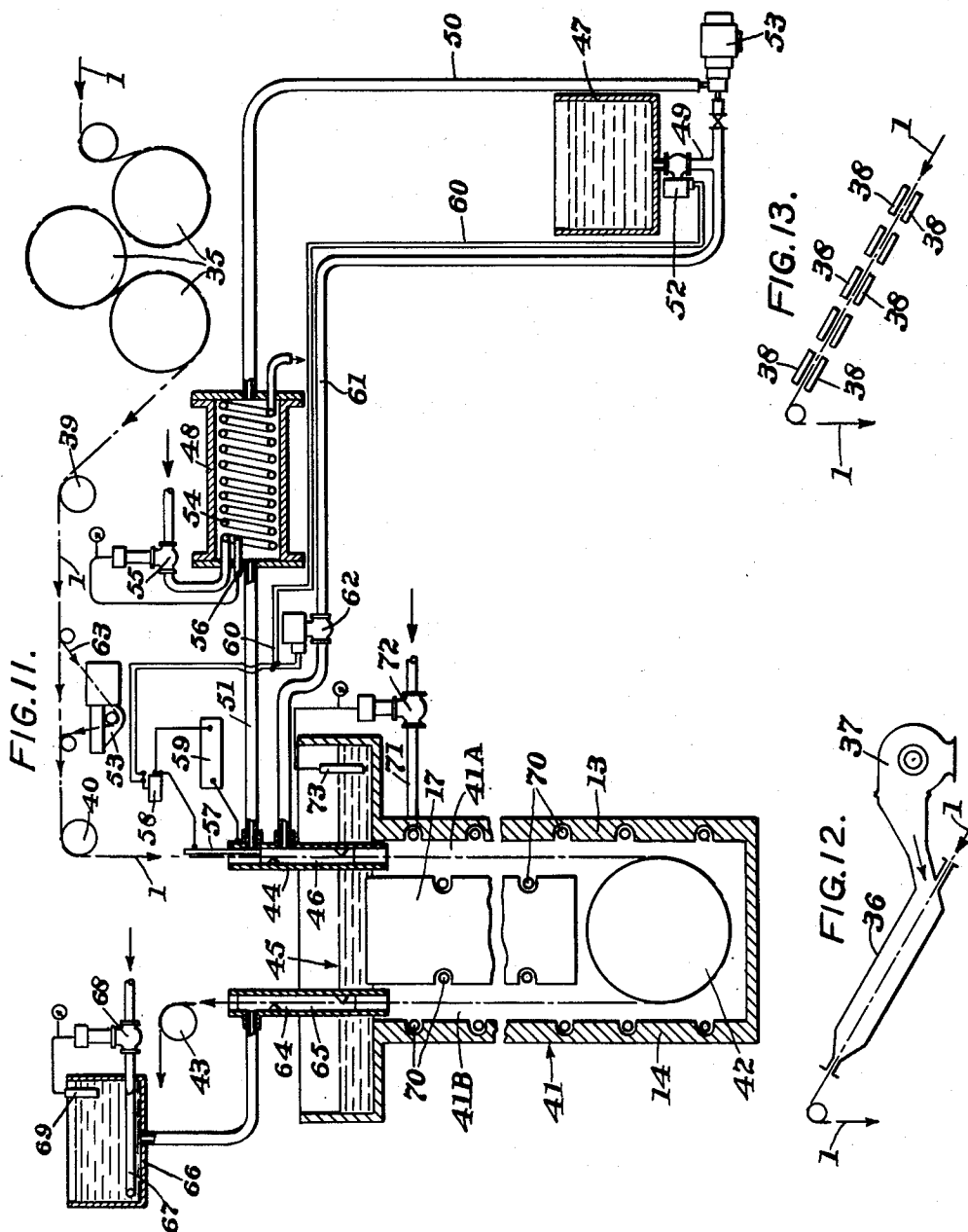
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PROCESS AND APPARATUS FOR DYEING OR PERFORMING RELATED
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Filed Feb. 3, 1954

5 Sheets-Sheet 5



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2,693,995

PROCESS AND APPARATUS FOR DYEING OR PERFORMING RELATED PROCESSES UPON TEXTILES USING MOLTEN METAL

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Application February 3, 1954, Serial No. 407,962

Claims priority, application Great Britain January 14, 1946

36 Claims. (Cl. 8—34)

The present application is a continuation-in-part of each of the following compending applications: Serial Number 722,042, filed January 14, 1947, which was allowed May 13, 1953, now forfeited; Serial Number 46,804, filed August 30, 1948, now abandoned; Serial Number 90,995, filed May 2, 1949, now abandoned; Serial Number 90,996, filed May 2, 1949, now abandoned; and Serial Number 90,997, filed May 2, 1949, now abandoned.

This invention relates to processes for the modification of textile materials by treatment with aqueous liquors at elevated temperatures and to apparatus for carrying out such processes. The term "textile materials" is intended to embrace various materials as used in the textile industries, for example, fabric, felt, yarn, or webs of material, including, for example, cotton, wool, linen, acetate-rayon, nylon, viscose, silk, cuprammonium rayon, "Orlon," a polyacrylonitrile fiber produced by E. I. duPont de Nemours & Co., "Terylene" and other natural or artificial materials, as well as glass fibers and material including the same. The term "textile" is not intended to restrict the scope of the invention to woven material. Such textile materials are characterized by possessing the property of being penetrable by conventional aqueous liquors used in dyeing and related processes, e. g., aqueous dye liquors and aqueous dye developing liquors.

This invention particularly relates to new dyeing methods and continuous dyeing apparatus.

FIELD OF THE INVENTION

The textile industry has many and varied processes for the treatment or modification of textile materials.

One general type of such treatment processes is that in which the textile materials are modified by treatment with aqueous liquors at elevated temperatures. This includes such operations as dyeing, moth-proofing, scouring, shrinking, size setting, rendering water-repellant, rendering crease-resistant, and the like. Each of the specific procedures which fall within the stated general type present special problems. This is especially true of those operations which come under the classification of dyeing.

As an example of problems associated with dyeing are the difficulties experienced in obtaining uniformity of color over the entire area of the goods. Thus, in the dyeing of cloth, for example, by a padding process, the cloth is usually passed through the dye liquor and subsequently through a mangle nip to express surplus liquor. Irregularities in the thickness of the cloth cause unequal squeezing with a tendency to express more liquor from the thicker than the thinner parts. This ultimately results in unevenness in coloration of the cloth.

Unevenness in coloration of fabric in dyeing procedures takes place also in the type of process where extrusion of dye liquor is effected by a suction extractor which depends upon the porosity of the cloth for the evenness of the results. This is also true in the case of a third dyeing process used in a dyeing jig or vessel in which the cloth is run through the liquor a sufficient number of times to obtain the desired result. However, because the control of this process is not easy due to difficulties of maintaining ideal conditions of volume, temperatures and dyestuff concentrations, uneven coloring is hard, if not impossible, to eliminate.

In operations in which textile materials are treated with aqueous liquors at elevated temperatures, heating of the material under treatment also presents serious problems. At present there are three main procedures employed to

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heat textile material. First is the type in which heat is transferred to the textile or like material by convection. Such operations suffer from the defect that air is required which contacts the materials and may adversely effect the treatment. Such operations are also costly and relatively inefficient.

Heating is accomplished by a second type operation in which a cylinder machine is employed and the material contacts the hot surface of the cylinder. Although such procedures are efficient from a thermal viewpoint, they suffer from the presence of air and in many cases cause an undesirable glazing of the surface of the cloth.

The third distinct type of heating operation uses radiant heating with heat being conveyed to the material by radiation. This type of operation is not only costly, but also suffers from the presence of air, particularly undesirable where dye liquors active with oxygen are used.

Most procedures used in the treatment of textiles with aqueous liquors at elevated temperatures also involve a step where pressure is applied to the textile material. For example, in dyeing, a pressure application step is generally required to remove excess of dyeing liquors or the like. The established practices for pressure application in this field use either rollers or flat plates. Aside from the problems of uneven pressure particularly with cloth of irregular thickness, as indicated above, such procedures generally result in some defacement of the surface of the material.

Aside from these problems which are experienced broadly in the treatment of textile materials with aqueous liquors, there are certain problems which are rather specific to the dyeing of textile materials. For example, the expense of the dyestuffs employed make it desirable to reduce the volume of unconsumed dye liquor remaining at the end of a run to a minimum. It is further desirable to enable accurate matching of shades with a minimum of effort and expense. It is still further of great benefit to avoid "tailing" difficulties without the use of a feed liquor of different composition from that of the original dyebath. Also, efficient commercial operation requires an ability to change dye baths with only a very small shut down time and to enable a great variety of treatment operations to be performed on the same equipment. Further, since most dyestuffs are of only limited solubility, it is a great advantage to be able to operate efficiently and satisfactorily with dye baths at elevated temperatures at which increased solubility of the dyestuff is achieved enabling more dyestuff and hence deeper shades to be attained in a single pass.

Other factors which may influence greatly the final results obtained in a dyeing operation include: the preparation which the cloth has received prior to dyeing, e. g., whether wetting agents or the like have been applied to the goods, the speed with which the cloth is run through the dyeing apparatus, the speed with which dyestuff liquors penetrate or are absorbed by the material under treatment, the adaptability of a particular process to treat materials composed of a variety of different filaments, i. e., union materials, and the ability of dye procedure results obtained on test or laboratory scale to be duplicated on a commercial scale.

OBJECTS

A principal object of this invention is the provision of new methods for the modification of textile materials by the treatment thereof with aqueous liquors at elevated temperatures and the provision of new apparatus for use in connection with such procedures. Further objects include:

1. The provision of new methods for dyeing textile materials.
2. The provision of new forms of dyeing apparatus.
3. The provision of new procedures for the treatment of textile materials with aqueous liquors at elevated temperatures which allow for uniform heating of the textile material, even with substantial variations in the thickness thereof, and at the same time eliminate air contact with the material during the high temperature treatment, all at low cost and at a high thermal efficiency.
4. The provision of aqueous liquor treatment operations for use with textile materials which permit the uni-

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form application of pressure thereto substantially independent of the thickness or configuration of the textile material under treatment.

5. The provision of new dyeing methods in which the volume of dyeing liquor per unit of cloth is maintained substantially constant during the critical stage of effective fixation of the dyestuff material upon the goods without evaporation of the dyeing liquor or similar variation thereof during said critical stage.

6. The provision of new dyeing operations in which a uniform quantity and strength of dye per unit of fabric is insured substantially independent of the configuration or thickness of the goods.

7. The provision of new dyeing procedures which enable deep shades to be applied with a single pass of the fabric through the dye liquor.

8. The provision of new dyeing procedures which are relatively independent of the prior treatment or preparation of cloth and which do not require superlative cloth preparation for satisfactory dyeing results.

9. The provision of new dyeing methods which are relatively independent of the speed with which the cloth being dyed is passed through the dyeing equipment and which allow cloth to be dyed at very high rates of speed, e. g., dyeing times of as low as two seconds.

10. New dyeing methods which permit extreme uniformity of shade or coloration to be obtained with all varieties of textile materials, even those which vary greatly in thickness throughout a given area.

11. The provision of new textile liquor treating apparatus which is comparatively simple in construction and easy to operate even for unskilled technicians.

12. The provision of new dyeing methods and dyeing apparatus which make possible the dyeing of union materials to give products having good uniformity of shade between the various fibers of the materials even when dyestuffs are employed which normally would give different depths of shade with the different fibers of which the union material is made.

13. The provision of new dyeing methods which make possible the use of increased temperatures to increase the affinity of the dyestuff for the fabric and the usable concentration of dyestuff in the dye liquor.

14. The provision of new dyeing operations and apparatus for use in connection therewith which makes possible the exclusion of air from the time the dyestuff on the cloth is in reduced form until the dyestuff has been maintained at elevated temperature for a sufficient time to substantially complete the fixation of the dyestuffs.

15. The provision of new apparatus for use in the dyeing of textiles which eliminates the use of pressure rolls or plates or similar mechanical squeezing or liquor expressing means.

16. The provision of textile dyeing apparatus which makes it possible to match the shades obtained on laboratory size apparatus without guess work or need for empirical adjustments when transferring to commercial or plant-size apparatus.

17. The provision of such apparatus and methods which make it possible to change from one dyeing shade to another substantially instantaneously and without need to discard large quantities of valuable dyeing liquors and which also permit "cleaning-down" to be done very simply.

18. The provision of such apparatus and methods capable of handling very large outputs of cloth at economically high speeds, e. g., speeds of 100 to 120 yards per minute, in a continuous fashion giving products of good shade-matching, uniformity, penetration and levelness throughout.

19. The provision of new methods and apparatus which enable dyeing with different classes of vat dyestuffs or of different sulphur dyestuffs, to be carried out simultaneously under the same conditions of temperature and alkali concentration in contrast to generally known procedures which are highly sensitive to temperature conditions and make it exceedingly difficult, if not impossible, to use certain vat dyes in conjunction with one another in a single dyeing.

20. The provision of dyeing methods which are usable with vat dyestuffs dissolved in an appropriate amount of alkali and reducing agent as well as the usual pigment padding type of operation in which the textile material is impregnated with an aqueous suspension of undissolved vat colors and subsequently treated in a vessel with an

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appropriate amount of alkali and reducing agent in order to solubilize the color in situ.

21. To enable the employment of aqueous treating liquors maintained as a floating layer upon a bath of molten metal at a temperature not greatly in excess of the melting point of the metal of the bath without encountering solidification of the metal of the bath which defaces the fabric being treated.

22. To enable high speed passage of textile materials through a molten metal bath the metal of which is solid at room temperature without encountering solidification of the metal of the bath.

23. To enable aqueous liquors which are adversely affected by elevated temperatures to be satisfactorily employed at these temperatures.

24. To enable prolonged continuous operation to be performed employing aqueous liquors containing hydrosulphite without encountering the formation of sludge on the surface of the molten metal bath.

25. To stabilize hydrosulphite containing aqueous liquors against the tendency of the hydrosulphite to decompose at elevated temperatures to form decomposition products which attack the metal of the molten metal bath and form a sludge.

26. To maintain the surface of the molten metal bath where the textile material enters the same free of air oxidation products without resort to the use of inert gases.

27. To avoid the tendency of the textile material to pick up particles of molten metal and sludge as it emerges from the molten metal bath.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

GENERAL DESCRIPTION

These objects are accomplished according to the present invention by the treatment of textile materials with aqueous liquors at elevated temperatures by floating a treating liquor on a bath of molten metal, passing the textile material downwardly through said floating liquor to impregnate the material with said liquor, then passing the textile material containing the treating liquor downwardly through said molten metal, continuing the passage of said material through the molten metal for a substantial distance to give uniform penetration of the liquor into said material by the uniform pressure of the molten metal effecting a squeezing action thereon, with said molten metal being heated to a temperature above about 60° C. and below a temperature at which any substantial ebullition of aqueous liquor from said cloth will take place, and finally passing said textile material out of said bath of molten metal with said textile material still containing a substantial portion of aqueous liquor therein. The molten metal is selected so that it does not chemically react with the textile material or the aqueous liquor thereon.

Preferably, the new method is employed for the dyeing of textile materials. In such cases, the dye liquor, or dye reducing liquor, as the case may be, is floated upon the surface of a bath of molten metal so that when the material under treatment leaves the floating layer and enters the molten metal bath, the material with the liquor carried with it may be passed downwardly to a substantial depth in the bath of molten metal and be subjected therein to elevated temperatures without any substantial evaporation of dyeing liquor from the textile material. Preferably the molten metal bath consists of Wood's or a similar low melting alloy of lead and bismuth having a melting point below about 100° C. and said metal is preferably maintained in molten condition at a temperature between about 80 and 100° C. Also, it is preferable to have the major portion of the path of the fabric through the molten metal vertical, or nearly so.

Further accomplishment of these objects is afforded by the provision of textile treating apparatus which comprises a substantially U-shaped chamber containing molten metal in the chamber having a melting point

below 100° C. and preferably above about 60° C. Lower melting metals such as mercury may be used, but, as is well known, it is dangerous to work with mercury in heated condition because of the noxious vapors which are emitted. The U-shaped chamber is provided with means for heating the metal in the chamber and container means are provided at the inlet of said chamber to receive aqueous treating liquors immiscible with said molten metal. The container is suitably shaped and positioned to permit the aqueous liquor supplied thereto to be floated as a layer on the surface of said molten metal. Preferably, such apparatus includes means for continuously feeding a continuous web of textile material into the inlet side of the chamber and means for withdrawing the continuous web from the outlet side of the chamber. In the more desirable forms of the apparatus, said aqueous liquor containing means consists of an open bottom trough positioned at the inlet end of the chamber with the lower end of the trough extending slightly below the surface of said molten metal bath and with a conduit connected to the trough for introducing the aqueous liquor onto the surface of the molten metal to float thereon.

While it is possible to successfully operate the new methods of this case as broadly described above, most satisfactory results are obtained when the liquor floating upon the molten metal is maintained at a very small volume on the surface of the metal bath with additional quantities of aqueous dye liquor being supplied thereto as it is absorbed by the textile material passing downwardly therethrough. Preferably, the floating liquor is employed in the form of an elongated vertical column with additional quantities of liquor being supplied to the column in substantially continuous fashion so as to maintain the height of the column uniform within a variation of 5%.

Moreover, when dyeing with vat or sulphur dye liquors a reducing agent such as sodium hydrosulphite is added to the floating dye liquor, or where the dye is first padded unreduced, the reducing agent is a part of the aqueous liquor which floats on the molten metal bath. In either event, prolonged heating of the aqueous dye liquor or aqueous dye reducing liquor leads to the formation of decomposition products which attack the molten metal with formation of sludge, and this may adversely affect the dyeing results on the material.

Still further, if the freezing point of the molten metal is not much lower than the maximum permissible temperature of the treating liquor, the temperature of the liquor must be maintained accurately and continuously in order to prevent solid particles of metal forming and interfering with uniform application of the liquor to the material. An aqueous liquor, for example, should not be above 100° C., while the freezing point of the molten metal may in some cases not be greatly below that temperature.

Accordingly, the layer of liquor floating on the molten metal bath is maintained at a very small volume by substantially continuously replenishing the floating liquor with fresh liquor which is heated from a temperature of about 25 to 30° C. to the temperature of the floating liquor, e. g., 80° C., just prior to being introduced to the layer floating upon the molten metal bath. Such procedure enables the floating layer of liquor to be maintained without variations in temperature, volume and strength of a magnitude likely to adversely affect the treatment and the length of time during which a hydrosulphite containing liquor is maintained at elevated temperature is kept short so as to reduce decomposition and resulting formation of sludge to a minimum. Still further, the temperature of the liquor in the floating layer is prevented from falling undesirably low.

Also if the textile material enters the layer of liquor floating on the molten metal in unheated condition, even if the floating liquor is itself heated, the textile material may still enter the molten metal bath at a temperature sufficiently low to solidify or "freeze" the metal of the bath. This may cause solid lumps or particles of the metal to be formed on the textile material at the interface between the metal and the dye liquor, and may interfere with the uniform application of the dye liquor to the material. This may also occur where the dyestuff is padded upon the textile material prior to entry of the padded material in the aqueous dye reducing liquor floating on the metal bath entry surface.

Accordingly, it is preferred to heat the textile material so that the material may enter the molten metal bath at a temperature above the freezing point of the metal bath. Naturally, the treating liquor floating on the surface of the metal bath is taken into consideration, and hence, the temperature of the material prior to treatment with the floating liquor should be such that the temperature of the combined textile material and treating liquor prior to entry to the metal bath is above the freezing point of the metal bath.

It is desirable, particularly when operating with vat dyestuffs in which the textile material is subjected to the action of liquors containing hydrosulphites, which treating liquor floats on the surface of the molten metal bath, to incorporate in the treating liquor an anti-oxidant substance which retards the rate of formation of alkali sulfides from the hydrosulphite. Reducing sugars, such as glucose, are particularly advantageous for this purpose.

Still further, it has been found that there is a tendency for the textile material as it leaves the molten metal bath to pick up scum or particles of the molten metal. To prevent this, an aqueous liquor is floated on the surface of the molten metal bath at the exit side where the textile material leaves the bath. The aqueous liquor which is floated on the exit surface of the molten metal bath is selected so that it is inert to the metal of the molten metal bath and is not deleterious to the dyeing liquor on the fabric. Additionally, the aqueous treating liquor floating at the exit may contain salts of other chemicals which assist the fixation of the dyestuff or neutralize the previously applied dye liquor. In this regard, when dyeing direct dyestuffs, the exit liquor may contain common salt, Glauber, or weak acids such as formic or acetic acid.

DETAILED DESCRIPTION

A more complete understanding of the new procedures and apparatus comprehended by this invention may be had by reference to the accompanying drawings in which:

Figure 1 is a diagrammatic side view of one form of the apparatus designed in accordance with the present invention.

Figure 2 is a vertical fragmentary transverse sectional view on an enlarged scale through the molten metal bath section of the apparatus of Figure 1.

Figure 3 is a fragmentary elevational view of one of the sides of the bath section shown in Figure 2.

Figure 4 is a cross-sectional view on the lines 4—4 of Figure 3.

Figure 5 is a perspective view of the means for maintaining aqueous liquor above the surface of the molten metal bath at the inlet side thereof.

Figure 6 is a sectional view on the line 4—4 of Figure 5.

Figure 7 is a sectional view diagrammatically illustrating a method in accordance with this invention wherein the material is shown as passing sinuously over a series of rolls immersed in a bath of molten metal.

Figure 8 is a sectional view diagrammatically illustrating a method in accordance with this invention wherein the molten metal bath comprises troughs arranged in tandem with the liquid level above the path of the material throughout, this view also showing filling blocks instead of correspondingly shaping the interior of the molten bath.

Figure 9 is a fragmentary elevation of open mesh wire gauze which may be used to line the sides of the molten metal bath in lieu of the narrow projections shown in Figures 3 and 4.

Figure 10 is a sectional view on the line 10—10 of Figure 9 showing the wire gauze anchored to the wall of a molten bath as by welding.

Figure 11 is a diagrammatic sectional side view of a modified form of apparatus in accordance with this invention showing the continuous treatment of a length of cloth with one form of a cloth heater, automatic means for heating aqueous dye liquor prior to automatically introducing it upon the surface of the molten metal bath and the provision of an aqueous liquor floating on the molten metal bath where the cloth emerges from the bath.

Figure 12 is a sectional detailed view showing cloth passing through another form of cloth preheater.

Figure 13 is a sectional detailed view showing cloth passing through yet another form of cloth heater for use in the apparatus of Figure 7.

Referring now to Figure 1, the cloth 1 is unwound from rolls 2 and is passed over rolls 3 directly into the bath indicated as a whole at 4 having a single entry pass at 4a and a single exit pass at 4b, around a bottom roll 5. The dyed cloth then passes away to roll 6.

Dyeing liquor is arranged to float on the surface of the metal bath, as will be more fully explained herein after in connection with Figures 2, 5 and 6. The level of the dye liquor is kept constant in the form of apparatus for controlling a supply of liquor from a main supply tank 8.

Cloth being treated in the apparatus of Figure 1 may take an alternative route as shown in dotted lines at 9 by passing through a padding trough 10 in order to take up dyeing liquor after which the cloth passes through nip rolls 11 down into the molten metal bath 4 as previously described. In this case, the level of the liquor in the trough 10 is maintained constant as by a float valve 10' which regulates the supply of liquor from a main supply tank 12.

The structure of the treating bath 4 is shown in more detail in Figures 2 to 6. As shown in Figure 2, the bath 4 comprises two vertical side plates 13 and 14 arranged closely together opposite each other and mounted upon a frame including base 15 and angular top members 16. A central partition 17 is provided between the side plates 13 and 14 dividing the apparatus into two separate vertical channels. This structure allows the molten bath proper to be maintained at a minimum of volume thereby requiring a minimum amount of the relatively expensive bath metal and requiring a minimum of heating.

The path of the cloth through the molten metal bath is indicated by 4a and 4b. Heat is communicated to the molten metal 18 at intervals throughout the whole of the bath by a series of steam pipes 18 located on each side of the cloth passageway throughout the entire length thereof. The molten metal intimately heats the cloth without chemically reacting therewith or with the dye liquor and furthermore it does not absorb the dye liquor. At the same time, the success of the present invention is due in part to the unique discovery that, if the cloth is maintained impregnated or wet with aqueous treating liquor during passage through the molten metal bath, which is achieved by floating the impregnating liquor on the molten metal bath, then molten metal is not absorbed by the cloth nor will the cloth be marked by the metal of the bath.

It will also be evident that utilization of molten metal not only enables simple, accurate and efficient application of heat, but, depending upon the depth and specific gravity of the molten metal bath, the pressure applied to the cloth may be controlled without increase in the pressure of the air surrounding the metal bath. In this way it is possible to impart to the cloth a uniform squeezing action of any desired pressure throughout the entire surface area of the cloth regardless of the irregularities in configuration or thickness of the cloth.

It is preferred to pass the cloth being treated through the molten metal bath in a substantially vertical elongated path. This is because it has been found that if the cloth is caused to move through the molten metal in a path other than substantially vertical, there is a strong tendency for the material to float upwards. This displacement of the material relative to a vertical route through the bath causes undesirable tension on the cloth and will produce marking of the cloth should the cloth rub against the walls of the bath. As those skilled in the art will appreciate, the vertical passage of the goods need not be absolutely so and there is no inherent objection to moving the material in a path slightly away from the vertical or in moving the textile-like material around the underside of a roller, such as roller 5 of the apparatus of Figure 1 or 2 as in such cases any flotation effect merely tends to keep the material in contact with the roller.

The top 19 of the bath 4 is of enlarged width and the surface of the molten metal bath is indicated at 20. Within this expanded region, there is located a dye box 22 provided with a downwardly extending, open-ended conduit 23 protruding into the molten metal bath. The dye box 22 may be integral with or removable from the bath vessel, and, as shown, is open at its upper end. The dye box 22 contains dye liquor 21. The cloth 1 passes into the dye box 22 through the open upper end thereof and into the layer of aqueous liquor contained therein, which is exposed to the atmosphere, and through the aqueous

layer to pass directly therefrom into the molten metal bath without exposure to the atmosphere.

As indicated in connection with Figure 1, the dye liquor is supplied to the dye box 22 by means of a control tank 7 and a float valve 7', the control tank being connected to the supply tank 8. Automatic means for maintaining the level of the molten metal bath constant may be provided also, if desired, but this is generally unnecessary since it has been found that loss of molten metal from the bath may be made negligible.

As can be seen from the drawings, the aqueous dye liquor or aqueous dye reducing liquor floats upon the surface of the molten metal bath. It has been discovered that by operating in this fashion the cloth contains a predetermined controllable quantity of aqueous liquor upon entry into the heated metal bath. This, along with the squeezing action of the molten metal bath controls the exact amount of treating liquor taken up by the cloth and at the same time air is excluded from the cloth from the time during the time the dyestuff on the cloth is in reduced form until fixation of the dyestuff has been substantially completed.

The treating bath 4 and the other sections of the apparatus, such as the dye liquor box 22, are formed relatively long in relation to their width so as to accommodate the entire width of cloth to be treated by the apparatus.

Figures 3 and 4 illustrate specific constructions for the walls 13 and 14 and central partition 17 designed to prevent binding of the cloth on the adjacent surfaces of the parts 13, 14 and 17. These means consist of internal narrow projections on the surfaces 13, 14 and 17 spaced by recesses, the recesses preferably being hydraulically interconnected. In this way, the molten metal may pass at all times between the cloth and the surfaces of the sides 13 and 14 and the central partition 17 so as to balance the pressure on each side of the cloth. This may conveniently be effected by providing elongated serrations extending from top to bottom of the bath proper on the surfaces 13, 14 and 17, the serrations being inclined slightly off the vertical, for example at about 2 1/2° as indicated in Figures 3 and 4. It has also been found desirable that these serrations on opposite faces should be inclined in opposite directions in order not to deflect the cloth. For example, if the serrations on the inner surface of 13 are inclined toward the right, then the serrations on the opposite inner face of the partition 17 are inclined towards the left. A similar arrangement is made upon the exit side of structure 4. As an example of dimensions, the serrations may be about 1/4" between their apices and with a depth of about 1/8".

The preferred form of the dye box 22 is shown in more detail in Figures 5 and 6. As can be seen, the dye liquor enters through inlet 24 and passes round to each longitudinal side of the dye box 22. The dye liquor enters the interior of the dye box through a series of holes 25 in each side of the box. The holes 25 increase in area from the near end to the remote end in order to equalize inflow along the length of the box.

In addition to or instead of heating the molten metal by internal pipes such as 18, the metal may be led externally through a heater and may also be filtered.

In a modification and referring to Figure 7 of the drawing, the bath 4 may comprise a series of rolls 30 substantially or wholly immersed in the bath of molten metal, the material passing thereover sinuously through the bath, the material travelling downwardly, laterally and upwardly as shown by the arrows in the molten metal bath; the rolls may thus fill a large proportion of the bath volume. As aforesaid, the treating liquor floats on the surface of the bath of molten metal.

It has been found that when cloth, for example, is passed through a bath of liquid metal as described above:

(a) A squeezing effect is obtained which depends on the specific gravity of the metal and the depth of the bath. The pressure is evenly distributed and does not deface the cloth.

(b) The metal positively prevents the escape of any treating liquor previously applied to the cloth and ensures that the whole of such liquor applied is in fact used for the process desired.

(c) The cloth and any liquor contained in it attain the temperature of the metal almost immediately and it is therefore possible to control the optimum conditions for the reaction.

(d) The exclusion of air during the process has the

effect of greatly accelerating and condensing the process if it is of a nature that is restrained by the presence of air.

(e) With a layer of treating liquor lying on top of the metal bath through which the cloth passes before entering the metal, a feature is that with non-uniform cloth the amount of liquor applied is proportional to the amount of cloth at any part, which is the condition required to obtain the best results.

(f) In the application of vat dyestuffs to wool the total amount of alkali available for producing damage of the fiber is restricted because of the low ratio of dye liquor to fabric; therefore a more universal use of vat dyestuffs for wool is permitted, and damage by the alkali is restricted.

As an example of the advantages quoted above, a heavy cotton fabric was pigment-padded with unreduced vat colors and passed through the usual reducing agents into a bath of mercury six inches deep at 110°. Development was complete in 30 seconds as compared to the 30 minutes to 1 hour necessary when the process is done in a vessel under hitherto existing methods.

Where a long immersion is required without the material contacting air, the molten metal bath may comprise troughs arranged in tandem, as shown in Figure 8, with the liquid metal level above the path of the material throughout and the material traveling downwardly, laterally and upwardly in the molten metal bath as indicated by the arrows.

The bath of molten metal required to apply the heat and pressure may be maintained at the minimum by inserting filling blocks 31 in the spaces in the bath not occupied by the material, instead of by correspondingly shaping the interior of the bath as described and shown above, suitable rolls 32 being provided over which the material passes from one trough to the next.

For textile printing, the color will be applied to the cloth prior to entry to the bath, in any known manner, and the cloth is then passed through the bath in similar manner to that indicated above, with the application of dye developing liquor at the surface of the metal bath.

Some examples of dyeing processes in accordance with the basic teachings of the invention as previously set forth will now be described.

For instance, Caledon Blue R. N. S., the vat dyestuff Indanthrene, Color Index 1106, normally dyed at 60° C. gave excellent results when dyed in the liquid metal bath at 108° C. Similarly, Caledon Red B. N. S., the vat dyestuff 1,2 Anthraquinonenaphthacridone, Color Index 1162, normally dyed at 20 to 25° C. also gave excellent results when dyed in the liquid metal bath at 108° C. Further, the amount of caustic soda required normally hitherto for Caledon Blue R. N. S. was about 6 gms. per liter and for Caledon Red B. N. S. about 2 gms. per liter. Both can now be dyed in the liquid metal bath aforesaid with the same quantities, and large variations in this quantity do not appreciably affect the results, no important difference being observed in either case within the range of 8 to 20 gms. per liter, the amount selected being independent of the nature of the dyestuff and solely dependent on the amount of reducing agent used. It thus becomes possible to mix vat dyestuffs of different classes in a common dyeing stage.

The invention is applicable to both of the types of dyeing of vat dyestuffs mentioned previously, e. g., application of the dye in reduced form or padding of the dye in unreduced form, followed by the application of a dye reducing liquor. However, the invention has the important advantage that when the dyestuff is applied in the reduced form, it is not essential that the whole of the color should be in solution when the fabric is impregnated.

Examples of the three abovementioned dyeings will now be described employing a low melting point alloy having a eutectic composition approximately as follows: tin, 13.3%; lead, 26.7%; bismuth, 50% and cadmium, 10%. This metal alloy has been found to be especially suitable for use as the molten metal and this composition has a melting point of about 70° C.

Example I

Dry prepared fabric is passed into the liquid metal bath (temperature 108° C.) through an aqueous dye-bath containing 100 gms. per liter Caledon Blue R. N. S., 10 gms. per liter Calsoline oil (Imperial Chemical Industries Limited), a highly sulphonated oil in aqueous solu-

tion, 200 gms. per liter caustic soda, 10 gms. per liter sodium hydrosulphite, 4 gms. per liter Formosul C. The passage through the liquid metal bath occupies fifteen seconds and a satisfactory shade is obtained. Compared with the normal method, there is a large saving in dyestuffs and chemicals.

Example II

Dry prepared fabric is passed into the liquid metal bath (temperature 108° C.) through an aqueous dye-bath containing 150 gms. per liter Caledon Red B. N. S., 10 gms. per liter Calsoline oil (Imperial Chemical Industries Limited), 20 gms. per liter caustic soda, 20 gms. per liter sodium hydrosulphite and 6 gms. per liter Formosul C, sodium sulphoxylate formaldehyde. A good dyeing is obtained in a passage occupying fifteen seconds.

Example III

Dry prepared fabric is passed into the liquid metal bath (temperature 108° C.) through an aqueous dye-bath containing 50 gms. per liter Caledon Blue R. N. S., 50 gms. per liter Caledon Red B. N. S., 10 gms. per liter Calsoline oil (Imperial Chemical Industries Limited), 20 gms. per liter caustic soda, 20 gms. per liter sodium hydrosulphite and 5 gms. per liter Formosul C. The passage, occupying fifteen seconds, produces the fast blue grey color which is to be expected in a combined shade of these two dyestuffs.

After oxidizing and soaping, all these dyeings possess the high standard of fastness to washing normally associated with this type of dyestuff.

Example IV

In a further example of the invention utilizing the metal alloy specified above as the bath medium, the alloy is heated to the temperature 102° C., the flat sides of the vessel being lined with 10 mesh steel wire gauze 33, as shown in Figure 9. Referring to Figure 10, the gauze is shown as being anchored to the wall of the molten metal bath in any suitable manner, as by welding at spaced points 34. Cotton fabric to be developed in this machine is first "pigment padded" on an ordinary two-roll padding machine with 60% squeezing, using an impregnating liquor containing 150 gms. Caledon Blue R. N. S., 30 ccs. Calsoline oil, and 80 gms. British gum, a degradation product of starch, (1:1) per liter. The impregnated fabric, undried, is passed into the molten metal bath through a bottomless box arranged at the surface of the bath with the lower edge immersed in the molten metal. Into this box is fed an aqueous developing liquor containing 45 gms. caustic soda, 60 gms. sodium hydrosulphite, and 10 ccs. Teepol X (Technical Products Limited), a detergent derived from mineral waxes, per liter, at a temperature of 60° C.

The flow of developing liquor to the box is adjusted in accordance with the absorption by the fabric, and the amount of developing liquor in contact with the fabric can be comparatively small. The passage of the fabric and feeding of the developing liquor serve to lower the temperature of the surface of the molten alloy so that ebullition of the aqueous developing liquor on contact is avoided. The passage of the impregnated fabric through the molten metal bath occupies 10 to 15 seconds, and the fabric when finally oxidized, washed, and soaped, is colored the full blue shade of excellent fastness normally associated with this dyestuff.

Example V

In a further example of the invention using the same apparatus described in the previous example for the application of sulphur dyestuffs, dry scoured cotton fabric is passed into the molten metal bath at 102° C., through an aqueous dye-bath containing 20 gms. Sulphol Khaki 2 G (200%), a sulphur dye, supplied by James Robinson & Co. Ltd., Huddersfield, England, 20 gms. caustic soda, 20 gms. sodium hydrosulphite, and 10 ccs. Teepol X per liter, supplied at 60° C. The cloth speed is adjusted to give an immersion time of 10 to 15 seconds in the molten metal bath. The dyed fabric is finally oxidized, washed and dried.

In the treating of yarns in accordance with the present invention, it is not necessary to maintain each yarn separate from the other and a reasonable amount of bunching together of the yarns is permissible. Yarn dyeing may be performed during the passage of the yarn to the beam

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from any convenient package and, if desired, in conjunction with sizing. In such a process the beam of yarn can be produced in a variety of colors by dividing the said bottomless dye box at the surface of the molten metal into sections.

Figures 11 through 13 illustrate a further improved form of apparatus incorporating additional refinements which have been discovered to give even more satisfactory dyeing of fabrics than the more basic and general form of apparatus illustrated in Figures 1 through 10.

In the form of apparatus shown in Figure 11, cloth 1 in continuous length passes in the direction of the arrows over steam cylinders 35 adapted to heat the heaviest cloth traveling at the highest speed to a temperature somewhat above 70° C. The apparatus may also be used for lighter cloth at lower speeds and the heating of the cloth may be controlled by varying the pressure of the steam upon the heating cylinders although this is not critical since overheating of the cloth is not serious when temperatures corresponding to 15 p. s. i. steam pressure are employed.

In Figure 12, an alternative arrangement for cloth heating consists of a casing 36 through which the cloth 1 passes and through which hot air is forced by a fan 37, the air temperature being such that the arrangement may be used for lighter cloth at lower speeds without concern for overheating.

In Figure 13, a further alternative arrangement for cloth heating consists of pairs of opposed electrical radiant heating units 38 spaced along the cloth length, the cloth passing between the units of each pair of radiant heating elements. Control of the cloth temperature is obtained by switching the radiant heating units on or off selectively.

The heated cloth 1 for the purposes of dyeing passes over the guide rolls 39 and 40 and directly down into the molten bath vessel 41 through the single entrance pass 41-A, around the bottom roll 42, out the single exit pass 41-B and away over the guide roll 43.

The dye box 44 comprises an open bottom metal box extending into the molten metal bath below the top surface 45 thereof and contains the dye liquor 46, which floats as a layer on the surface 45 of the molten metal.

The layer of liquor 46 is maintained at a comparatively small volume and as it is absorbed by the cloth passing through the apparatus, it is substantially constantly and automatically replenished with fresh liquor heated to the temperature of the liquor 46 in order to maintain the condition of the liquor in said layer such that variations in temperature, volume and strength of a magnitude likely adversely to affect the treatment are avoided.

The replenishing liquor is heated as it is supplied to said layer. In this way the treating liquor is heated and is very quickly thereafter absorbed by the textile material. Thus, prolonged heating and formation of scum is avoided. Moreover, the temperature of the liquor is maintained substantially constant and is prevented from falling undesirably low.

This control of aqueous liquor supply is accomplished through a liquor preheater arrangement comprising a supply tank 47, a small capacity heating tank 48 and connecting pipes 49, 50 and 51. An electrically controlled feed valve 52 is positioned on conduit or pipe 49. Liquor admitted by the control valve 52 and also present in the lines 49, 50 and 51 is circulated through the apparatus by the pump 53. As the level of the liquor 46 in the dye box 44 drops, control valve 52, in a manner to be described more fully hereinafter, is opened in order to allow entry of more liquor into the system to pass to the heating unit 48 and thence to the dye box 44.

The liquor in the heating tank 48 is heated by a coil of tubing 54 supplied with steam from a thermostatically controlled steam valve 55, the thermostat having control contacts 56 in the heat exchanger 48. As shown, the contacts 56 are positioned on the discharge side of the heating tank 48.

The aqueous cloth treating liquor in the supply tank 47 is maintained at a relatively low temperature of preferably 25° to 30° C. Through the action of the control valve 52 and the heating means 48, the liquor is only heated just prior to its passage into the dye box 44 up to a temperature of about 80° C. Thus, the liquor is at this elevated temperature for only a short period before it is absorbed by the cloth 1 passing therethrough.

The liquor feed control valve 52, mentioned above,

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is regulated by the level of the liquor 46 in the dye box 44. This is accomplished as follows:

The dye liquor layer 46 may be maintained at any desired average depth, for example 12 inch, and with a cloth width of, for example, 50 inches, only a relatively small quantity of about ½ to 1 gallon of dye liquor is in use in the dye box 44 in contrast with the 30 to 60 gallons normally used such as in a dye jig. An adjustable metal rod 57 projects down into the dye box 44. The rod 57 is connected through a relay 58 to an electric battery 59 which in turn is connected to the dye box 44. The electrical actuation or tripping of the relay 58 operates the liquor feed valve 52 which is connected to the relay 58 by leads 60. When the level of the liquor in the dye box 44 rises and contacts the metal rod 57, the circuit operates to close the feed valve 52, the rod acting as an electrical conductor, and when the liquor drops down below the end of the metal rod 57, the feed valve, in turn, is opened. In this fashion a substantially constant level of liquor 46 is maintained in the dye box 44.

It is found that the caustic solution of the dye liquor is liable to form froth on the liquor surface and as these froth bubbles act as conductors in the same manner as the liquid to give a possible false indication of liquor level, a small quantity of turpentine or other suitable liquid, e. g., hydrocarbon, may be floated on the surface of the dye liquor 46. This eliminates frothing and causes the relay 58 to be actuated only by the true liquor level.

As the avoidance of any localized overheating of the liquor depends on the rate of the liquor flow, and since the liquor flow from the tank 48 may be required to cease temporarily, a conduit 61 is provided which connects the dye box 44 with the conduit 50 through the electrically controlled valve 52 and the connecting pipe 49. A circulation valve 62 in the conduit 61 is electrically controlled by the relay 58 which operates to open the valve 62 when the valve 52 is closed and vice versa. In this manner, the liquor flow through the heater 48 is constantly maintained.

As indicated in dotted lines at 63, the cloth 1 may, in addition to passing through the liquor 46, pass through a trough 53 in order to take up aqueous treating liquor. In this case, the level of the liquor in the trough 53 is maintained constant and is supplied from a main supply tank (not shown). The trough 53 may be located to receive the cloth prior to the heating on the cylinders 29, if desired. As an example of relative values in the operation of the process, with the metal bath at 90° to 95° C. and with a treating liquor 46 floating thereon at about 80° to 85° C., the cloth 1 should be preheated so that upon entering the treating liquor 46, the cloth temperature is such that the temperature of the combined cloth 1 and treating liquor 46 is not less than 75° C. For example, a textile material 1, having a specific heat of 0.3, absorbs 130% by weight of treating liquor 46 having a specific heat of 1.0 at 80° C. and should enter the treating liquor at 72° C. if the combined temperature is to be 78.5° C.

It is desirable to maintain the temperature of the molten metal bath at no greater than 90° to 100° C., since at higher temperatures with the aqueous treating solutions, steam may be generated below the surface of the molten metal and passed up through the metal bath and interfere with the even application of the dyeing liquor and cause streaky dyeing. Furthermore, it has been discovered that if the molten metal treating process is operated so that the cloth upon passage through the molten metal bath becomes substantially freed of treating liquor in the liquid phase, molten metal will be absorbed by the cloth and also any scum which may have a tendency to form upon the molten metal bath will be occluded by the cloth as it emerges from the molten metal bath. When this transpires, unsatisfactory results are obtained.

The cloth upon emerging from the molten metal bath, passes through a box 54 which is open at both ends and which projects into the molten metal bath. The box 64 contains an aqueous liquor 65 which floats on the surface 45 of the molten metal. The aqueous liquor 65 is supplied to the box 64 by gravity from a tank 66 heated by the steam pipes 67 to which steam is introduced in controlled quantities through a valve 68 regulated by a thermostat having its terminals 69 projecting into tank 66. The solution in the box 64

is maintained at constant level by overflowing on to the surface 45 of the molten metal. As in the case of the apparatus shown in Figure 2, the molten metal treating bath 4 of the apparatus of Figure 7, consists of two side members 13 and 14 and a vertical center partition 17. Along the vertical sides and within recesses, there are located heating elements such as the steam pipes 70 which in the form of apparatus of Figure 11 are fed through the pipe 71 which is controlled by the valve 72 through the thermostat control 73 which projects down into the molten metal bath below the surface 45.

The following further illustrative examples of actual operations conducted in accordance with the procedures of the present invention are given in order to provide a further understanding of the details thereof.

Example VI

This example illustrates the vat dyeing of cotton fabric. In addition, it illustrates also the vat dyeing of viscose and linen fabrics.

Cotton fabric which has been dried after scouring and bleaching is passed from a bulk roll thereof on to heating cylinders where the fabric leaves a space of about 7 feet from the last heating cylinder into a dye bath 8 inches deep which floats on the surface of molten metal alloy contained in a U-shaped vessel with legs 5 feet deep. The fabric on entering the dye liquor has a temperature of 75° C. The metal alloy contained in the U-shaped vessel has a eutectic composition of approximately 13.3% tin, 26.7% lead, 50% bismuth, and 10% cadmium and possesses a melting point of about 70° C.

The dye liquor indicated as floating on the molten metal surface, is made up and stored at room temperature (20° C.) and is pumped to the dye bath on the surface of the molten metal through a dye-preheater which heats the dye liquor to 75° C. within a few minutes of its absorption by the cotton fabric.

The dye liquor employed has the following composition: 150 gms./l. of the vat dyestuff 3', 4'-dichloro-1, 2-anthraquinone acridone (Color Index 1161) as sold commercially by I. C. I. Ltd. as "Caledon red violet 2 R. N. S." 2 gms./l. "Calsoline oil" supplied by I. C. I. Ltd.

20 gms./l. sodium hydroxide
30 gms./l. sodium hyrosulphite
15 gms./l. glucose

The molten metal is maintained in the treating bath at a temperature of 95° C. by automatically controlled heaters. Likewise the supply of the dye liquor to the surface of the metal and the temperature thereof are automatically controlled.

The fabric is passed at a speed of 80 yards per minute giving an immersion time for the 8 inches of dye bath of 0.17 second and for the 10 foot passage through the molten metal of 2.5 seconds. The preheated fabric on passage through the dye bath absorbs dye liquor. Then upon entering the molten metal it has excess dye liquor squeezed uniformly out of it while at the same time the impregnated fabric is heated to an elevated temperature in the absence of air.

The fabric emerges from the molten metal into a 10 percent aqueous solution of Glauber's salt which floats on the surface of the molten metal at the exit side of the U-shaped vessel. The fabric emerging from the Glauber's salt bath is rinsed, oxidized and soaped in known manner using the conventional open width soaping range.

The resultant cotton fabric is colored a uniform reddish violet shade of excellent fastness.

Operating in similar fashion, viscose and linen fabrics are dyed to give products of reddish violet shade of excellent uniformity throughout the entire surface thereof and of good light fastness.

Example VII

This example illustrates the vat dyeing of cotton-viscose union fabric.

Cotton-viscose fabric which has been scoured, bleached and dried is dyed using a process as described in Example VI, but with the following dye liquor:

50 gms./l. of the vat dyestuff, trichloro-N-dihydro-

1,2,1,2'-anthraquinoneazine (Color Index 1114) as supplied by I. C. I. Ltd. as "Caledon Blue R. C. S." 2 gms./l. of a sulphated fatty acid ester wetting and dispersing agent such as Alcopol T sold by Allied Colloids Ltd.

6.6 gms./l. sodium hydroxide
10 gms./l. sodium hydrosulphite
5 gms./l. glucose

The fabric speed is 60 yards per minute giving an immersion of 0.22 second in the dye bath and 3.3 seconds in the molten metal bath. The resulting union fabric, after oxidization and soaping, is colored a medium blue and has excellent fastness.

Example VIII

This example illustrates the vat dyeing of linen fabric using a so-called pigment padding technique.

Linen fabric which has been scoured and bleached is impregnated using a suspension of vat dyestuff in a two bowl padding mangle in known manner. The dye suspension contains:

300 gms./l. of the vat dyestuff dimethoxy-dibenzanthrone (Color Index 1101) as supplied by I. C. I. Ltd. as "Caledon Jade Green X. N. S." 10 gms./l. "Calsoline oil"

The impregnated fabric is squeezed to leave 70 percent of liquor in the fabric and is dried in a hot air drying machine.

The dyestuff in the fabric is fixed thereon by passing through the molten metal machine in the manner described in Example I, but instead of the dye liquor of Example VI, a developing liquor of the following composition is introduced upon the surface of the molten metal bath and the impregnated fabric passed there-through:

20 gms./l. sodium hydroxide
30 gms./l. sodium hydrosulphite
2 gms./l. of a sulphonated fatty acid ester wetting agent
15 gms./l. glucose.

The fabric is passed through the machine at 60 yards per minute. The resulting fabric after further oxidation and soaping is colored a fast full green shade which is uniform in depth and appearance throughout the entire length of the fabric.

Example IX

This example illustrates the dyeing of cotton fabrics with sulphur dyes. It also illustrates the dyeing of viscose and linen fabrics with the same type of dye.

Cotton fabric of the pile type having a design woven into the pile, such as fabric used for drapery material, which has been scoured, bleached and dried, is treated according to the method described in Example VI, with the exception that the following dye liquor is employed:

40 gms./l. of sulphur dyestuff of the trade name "Thional Navy Blue R. M. S." sold by I. C. I. Ltd. which is a sulphur dyestuff of the Immedial Direct Blue RL type, the production of which is described in the B. I. O. S. Final Report No. 983, Manufacture of Thioindigo and Sulphur Dyestuffs, page 85 (P. B. No. 79,226)
13 gms./l. sodium hydroxide
20 gms./l. sodium hydrosulphite
2 gms./l. of sulphonated oil wetting agent
10 gms./l. glucose

The cotton fabric is fed through the apparatus at a speed of 50 yards per minute and after oxidation and rinsing of the fabric, a product having a deep navy blue shade is obtained.

In similar fashion dry, scoured, and bleached viscose and linen fabrics are dyed with comparable results.

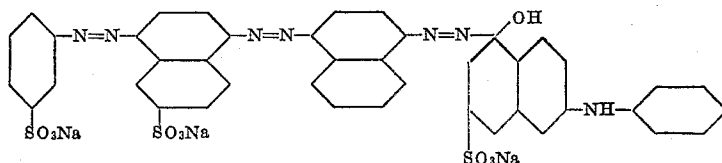
Example X

This example illustrates the dyeing of cotton fabric with direct cotton dyes. It also illustrates the dyeing of viscose and linen fabrics with the same type of dye.

Cotton pile toweling which has been dried after scouring and bleaching, is treated in the apparatus as described in Example VI. The fabric is not preheated before passing into the dye bath and the dye liquor is made up and stored at 80° C. Before introduction on to the surface of the molten metal bath, the dye liquor is preheated to a temperature of 100° C. The

molten metal bath is maintained at a temperature of 103° C.

The dye liquor used has the following composition:
5 gms./l. of direct cotton azo dye, "Chlorantine Fast Blue 4 GL" such as sold by Clayton Aniline Company of Manchester, England. This dye has the following formula:



2 gms./l. of sulphated secondary fatty alcohol
10 gms./l. Glauber's salt.

The fabric is passed through the apparatus at a speed of 40 yards per minute. Upon emerging from the salt bath at the exit end of the apparatus, the cloth is rinsed to yield a product having a uniform medium blue color.

Operating in similar fashion, viscose and linen fabrics are dyed in identical fashion to give comparable results.

Example XI

This example illustrates the dyeing of spun viscose fabric with direct dyes. It also illustrates the dyeing of cuprammonium rayon fabrics with such dyes.

Dry scoured viscose fabric is dyed using the procedure described in Example X, but with a dye liquor of the following composition:

10 gms./l. of direct cotton dyestuff, the sodium salt of p - sulphobenzene-azo - benzene - azo - 6 - benzoylamino-1-naphthol-3-sulphonic-acid (Color Index 278) sold by I. C. I. Ltd. as "Chlorazol Fast Red K"
2 gms./l. of sulphated secondary fatty alcohol wetting agent
10 gms./l. sodium chloride

The fabric after rinsing following the dyeing treatment is uniformly red throughout.

In another case, cuprammonium rayon fabric is dyed by the same procedure and with comparable results.

Example XII

This example illustrates the dyeing of wool fabric with vat dyes. It also illustrates the dyeing of wool-union fabric and natural silk fabric with vat dyes.

Heavy wool napped fabric which has been scoured and dried is preheated to 85° C. by passage through a radiant heat unit after which it is passed through a dye bath floating upon a molten metal bath such as described in Example VI. A dye liquor having the following composition is used:

30 gms./l. of "Caledon Red B. N. S." sold by I. C. I. Ltd.
5 gms./l. of sulphonated oil wetting agent
4 gms./l. sodium hydroxide
6 gms./l. sodium hydrosulphite
5 gms./l. glucose.

The fabric is passed through the machine at a rate of 40 yards per minute and after developing, oxidizing and soaping of the fabric, a cloth dyed a fast red color is obtained. No apparent damage to the wool fabric due to contact with hot strong alkali can be observed.

In similar fashion, natural silk fabric is dyed a fast red color.

Example XIII

The procedure of Example XII is repeated using dye liquor of the following composition:

100 gms./l. of the vat dye dimethoxy-dibenzanthrone (Color Index 1101) such as sold by I. C. I. Ltd. as "Caledon Jade Green R. N. S."
5 gms./l. sulphonated oil wetting agent
5 gms./l. sodium hydroxide
50 gms./l. sodium silicate
20 gms./l. sodium hydrosulphite
10 gms./l. glucose

Fabric speed with both the wool fabric and natural silk fabric is 40 yards per minute and in each case the fabric is dyed a uniform green color.

Example XIV

This example illustrates the dyeing of wool fabric with acid dyes. It also illustrates the dyeing of wool-union and natural silk fabrics with acid dyes.

Wool suiting material is preheated to a temperature of 95° C. by passage through a hot air drying machine

and then passed into the dye apparatus as described in Example VI.

In the apparatus a dye liquor having the following composition is employed:

5 gms./l. of wool dyestuff, the sodium salt of p-sulphobenzene-azo-beta-naphthol (Color Index 151) such as "Orange II" supplied by L. B. Holliday & Company
10 gms./l. of sulphated secondary fatty alcohol wetting agent

The dye liquor is made up and stored at 100° C. and supplied to the surface of the molten metal bath at a temperature of 100° C. while the molten metal bath is maintained at a temperature of 98° C. The fabric is passed through the apparatus at a speed of 20 yards per minute giving an immersion time of 0.66 second in the dye bath and 10 seconds for passage through the molten metal bath. At the exit end, an aqueous bath consisting of a 1% aqueous solution of acetic acid maintained at 95° C. is floated on the molten metal bath.

Following exit from the acetic acid bath, the fabric is rinsed in hot water continuously in known manner and then dried. Cloth uniformly dyed an orange color is obtained.

The same operation is repeated using wool-union fabric and natural silk fabric with comparable results in color, shade and uniform coverage.

Example XV

Example XIV is repeated substituting the following dye liquor:

5 gms./l. of acid dye, the sodium salt of 4-p-sulphobenzene - azo - 1 - o - m - dichloro - p - sulphophenyl - 3 - methyl-5-hydroxy pyrazol (Color Index 639) such as "Xylene Light Yellow 2G" supplied by Sandoz Chemical Company.
10 gms./l. of sulphated secondary fatty alcohol wetting agent
10 gms./l. formic acid (80%)

The fabrics, following hot water washing and drying, possess a uniform yellow color.

Example XVI

This examples illustrates the dyeing of wool fabrics, wool-union fabrics and natural silk fabric with soluble acetate dyes.

The process described in Example XIV is repeated using the following dye liquor:

5 gms./l. of soluble acetate dye such as Solacet fast orange, 2 G. K. S. as sold by I. C. I. Ltd. which is a water-soluble disazo dye
10 gms./l. of sulphated fatty alcohol wetting agent
10 gms./l. boric acid

An orange colored fabric of uniform shade is obtained following hot water rinsing and drying, upon exit from the treating apparatus.

Example XVII

This example illustrates the dyeing of cotton, viscose and linen fabrics with basic dyes.

Cotton duck material is mordanted in known manner with tannic acid. After drying of the fabric, it is heated to 75° C. by passing over steam heated cylinders and is then passed into apparatus such as described in Example VI through dye liquor floating on the surface of the molten metal bath maintained at a tem-

perature of 95° C. The dye liquor possesses the following composition:

- 5 gms./l. of the basic dye, tetramethyl-diamino-diphenazthionium chloride (Color Index 922) such as "Methylene Blue 2B" supplied by I. C. I. Ltd.
- 10 cc. per liter methylated spirits

The dye liquor is made up by pasting the dry dye-stuff with the methylated spirit and is then diluted to required volume with cold water. The dye liquor is stored cold and just prior to floating upon the surface of the molten metal bath, it is heated to 75° C. by passing through a preheater.

The fabric is passed through the dyeing apparatus at 30 yards per minute and leaves the molten metal bath through a water bath of 95° C. floating on the exit side of the molten metal. The fabric after drying has a uniform blue color.

The identical procedure is followed with viscose and linen fabrics with comparable results.

Example XVIII

The example illustrates the dyeing of cellulose acetate rayon and polyester ("Terylene") fabrics with dispersed acetate dyes.

Dry, scoured cellulose acetate rayon fabric is passed from a bulk roll through a hot air dryer where it is heated to a temperature of 75° C. and from there into a dye bath floating on the surface of a molten metal bath in apparatus such as described in Example VI. The dye liquor through which the cloth passes possesses the following composition:

- 10 gms./l. of acetate dye "Duranol Red X3 B 300" powder as sold by I. C. I. Ltd. which is an amino-anthraquinone derivative
- 5 gms./l. soap flakes

The dye liquor is made up and stored at 75° C. and is pumped to the dye bath container on to the surface of the molten metal at this temperature. The fabric is passed through the dye and through the molten metal which is maintained at a temperature of 99° C. at the rate of 30 yards per minute. It leaves the molten metal through a bath of hot water floating upon the exit surface of the metal.

After rinsing of the fabric upon exit from the hot water bath (95° C.), the fabric is found to possess uniform shade and to be dyed a bright red.

Example XIX

In this example, nylon is dyed with dispersed acetate dyes. Nylon fabric is scoured and then dried following which it is processed by the procedure described in Example XVIII using the following dye liquor:

- 10 gms./l. of dispersed acetate dye "Duranol Brilliant Yellow 6 G 300" powder such as sold by I. C. I. Ltd. which is an aminoanthraquinone derivative
- 5 gms./l. soap

The fabric is passed through the dye apparatus at a speed of 30 yards per minute and upon being washed and rinsed, following the dyeing operation, possesses a good yellow shade.

Example XX

This is an example of the use of the present invention for dyeing of nylon with acid dyes.

Dry, scoured nylon fabric is dyed according to the method described in Example XVIII using the following dye liquor:

- 10 gms./l. of the acid dye, the sodium salt of benzene-azo-beta-naphthol-6, 8-disulphonic acid (Color Index 252) such as "Croceine Scarlet 3 B" sold by I. C. I. Ltd.
- 10 gms./l. formic acid (80%)
- 1 gm./l. sulphated fatty secondary alcohol wetting agent

The dye liquor is made up and stored at 95° C. and is pumped to the dye liquor chamber at the surface of the molten metal bath at this temperature. The nylon fabric is passed through the apparatus at the speed of 20 yards per minute giving an immersion time of 0.66 second in the dye liquor and 10 seconds in the molten metal.

Upon emerging from the apparatus, the nylon fabric is rinsed and dried. A material which is uniformly colored scarlet throughout the entire length thereof is obtained.

Example XXI

This example illustrates the dyeing of both nylon and orlon fabrics by vat dyes.

Nylon fabric which has been scoured and then dried is processed continuously by the procedure described in Example I using, however, the following dye liquor:

- 30 gms./l. of thioindigoid vat dyestuff such as Durindone Pink F. F. S. as sold by I. C. I. Ltd. which is 6,6'-dichloro-4,4'-dimethylthioindigo.
- 2 gms./l. sulphonated oil wetting agent
- 15 gms./l. sodium hydroxide
- 15 gms./l. sodium hydrosulphite
- 15 gms./l. glucose

The cloth is processed at a rate of 20 yards per minute and following the usual oxidation, soaping and rinsing steps, nylon fabric having the expected pink color is obtained.

In another case orlon fabric is processed in an identical way with comparable results.

Modifications

The type of metal used in the essential metal bath is important to the success of the present invention. There are a number of usable metals but those most desirable have a melting point between 60° and 100° C. and especially between 60° and 80° C. The most satisfactory metals of this type for the purpose are lead and bismuth-containing eutectic alloys such as Wood's alloy, Rose's alloy and the like. A particularly desirable specific alloy is described in the examples.

Many types of aqueous liquors may be used in carrying out the new processes. Although better results are obtained with some formulations of the liquors than with others, wide variations in the concentrations, types and combinations of ingredients present in the treating mixtures may be used. Obviously, the aqueous liquors should not include ingredients which are reactive, in the concentrations used, with the metals contained in the bath, for example, heavy metals such as lead, bismuth, tin, cadmium or the like.

Dyestuff solutions or suspensions comprise the aqueous liquors, however, most useful in the new operations. The usable dyestuffs include all those known to be useful in dyeing organic filaments. This includes vat, sulphur, direct, acid, and all other general types of dyes. As a matter of fact, one of the primary advantages of the present invention is its ability to be used with so many different classes of dyestuffs, with equally fine results. As those skilled in the art know, vat dyestuffs are generally grouped into three separate classes depending upon the particular temperature range that has been required to be used in the past with the dyestuffs in dyeing. Such groupings are substantially nullified, however, by the present invention because virtually all vat dyes may be successfully used in the new operations at one and the same temperature range, e. g., 90° to 100° C.

Numerous specific dyes are mentioned in the foregoing examples and there is no need to list more here because of the extreme variety which may be employed.

When dyeing liquors are employed, they may include supplemental ingredients as is well known in the art. These include wetting agents, emulsifying agents, dispersing agents, inorganic and organic salts and acids, soaps, syndets, gums, colloids, corrosion inhibitors, organic solvents, developing agents and the like. Specific substances are given in the foregoing examples and since there are so many more which can be used and will be apparent to those skilled in the art, a further detailed list here is unnecessary.

Other reagents which may be included in the aqueous treating liquors, either alone or in mixture with themselves or any of the above, include moth-proofing agents, crease-proofing agents, scouring agents, sizes, water-repellant producing agents and the like. These are all well known in the art and they are all generally applicable to the new operations.

Concentrations and ratios of the reagents in the aqueous liquor and not critical. Those amounts generally employed with prior known procedures or comparable amounts as required by the particular textile material being treated may be used. The foregoing examples illustrate this feature of the invention sufficiently to enable anyone skilled in the art to adapt the new operations to any special case.

The depth or other dimensions of the aqueous treating liquor bath are not critical and may be varied. Since all or a section of the aqueous liquor is floated upon the surface of the molten metal bath, a certain practical limit is imposed upon the aqueous bath depth due to the hydrostatic head which may be supported, but this always has been found sufficient in actual operation. Usable depths of aqueous liquor floating above the molten metal bath may be from about 1 inch to about five feet, although shorter or much longer depths may be used. The width and length of the aqueous baths will be varied to accommodate the size of the textile material under treatment. It is desirable to make the aqueous bath, however, as small as possible, so that a minimum of treating liquor will be required. In this regard, a depth of 8 to 12 inches, a width of one inch and a length just slightly longer than the width of the fabric to be treated are preferred dimensions. This allows for saving in material, control in uniformity of temperature and strength as the operations progress, and permits faster change-over.

In those operations where an aqueous treating liquor containing a hydrosulphite is used, the liquors preferably include an anti-oxidant. This helps to inhibit formation of sludge on the surface of the metal bath. Reducing sugars, e. g., glucose, are preferred, but other suitable agents include aldehydes, e. g., benzaldehyde, and tannic acid.

The function of the antioxidant is to inhibit the tendency of the hydrosulphite to decompose to form products which attack the metal of the bath. Very small amounts of suitable antioxidant will accomplish this purpose and the minimum quantity necessary can be determined by simple observation. Since the deleterious decomposition is a function of many factors, e. g., proportion of hydrosulphite, temperature of operation and the time during which the hydrosulphite is maintained at the elevated temperature, no precise minimum proportion of antioxidant can be presented. Since suitable antioxidants are quite mild, they do not interfere with the solubilization of any ordinary vat or sulphur dyestuff even when the antioxidant is employed in quantities as large as the quantity of hydrosulphite employed. Such large quantities are far more than required for any conceivable dyeing or dye reducing operation.

Temperature of the aqueous bath during treatment of the textile material is important. When the aqueous liquor is floating upon the metal bath, it should be above the melting point of the metal and below its own boiling point, and preferably, between 80° and 100° C. Where a temperature sensitive liquor is employed, such as is the case of various dye liquors which deteriorate upon standing at elevated temperatures, the liquor is best heated just prior to being floated upon the metal bath. Thus, the liquor may be stored at room temperature (about 20° C.) and then heated in suitable fashion on the way to the bath container to about 80° to 100° C.

The temperature of the molten metal bath is also important. Obviously, it must be above the metal melting point. Also, it should be below the temperature at which ebullition of the aqueous liquor takes place as the cloth passes therethrough. This may be as high as about 103° to 105° C., or higher, due to the high pressures in the metal bath and the cooling effect of the aqueous liquor and the cloth upon the upper region of the molten metal bath at the entrance end. Preferably, the temperature of the metal bath is about 80° to about 100° C.

The process is operated in best fashion when an aqueous liquor also floats upon the exit surface of the metal bath. It has been found that the presence of an aqueous layer where the textile material emerges from the molten metal bath greatly reduces the tendency of the textile material to pick up particles of the molten metal. This has been discovered to greatly improve the results apparently due to several reasons. First, it insures that the cloth as it leaves the metal bath will remain wet with aqueous liquor. This appears to keep metal from the bath from being picked up and carried along with the cloth and to prevent streaks, blotches or the like, from forming on the cloth. Also, the exit floating liquor reduces scum formation on the metal bath, and accordingly, the textile material does not leave the molten metal bath with particles of scum clinging thereto.

The nature and composition of the exit floating bath is not critical. Generally, it is a salt solution, e. g., Glauber's salt, sodium chloride, etc., but it may be any other desired aqueous liquor of a character adapted to assist or complete the treatment being carried out in the transit through the metal bath, or of a character calculated to assist any subsequent treatment. Clearly, the exit liquor could also be neutral, for example, plain water. The same comments regarding reagent concentrations, ratios, temperature and the like made relative to the inlet floating aqueous bath apply to the exit bath.

It has been discovered that when dyeing with vat or sulphur dyestuffs, the exit liquor quickly becomes contaminated with caustic soda and hydrosulphite. The tendency of this alkaline exit liquor is to strip some of the dye already applied to the material, thereby giving a streaky effect. To overcome this particular defect, the exit liquor may consist of a strong solution of common salt or Glauber salt, fresh solution being added as necessary to maintain the exit liquor in a condition so that it does not substantially affect the previously applied dyestuff.

Further, when dyeing with vat or sulphur dyestuffs, the exit liquor should not be made acidic since under acid conditions, hydrosulphite decomposition products attack the metal to form a sludge. The formation of sludge where the textile material emerges from the molten metal bath causes adherence of sludge and metal to the textile material and thereby causes faulty treatment, for example, patchy dyeing, and loss of metal.

The floating liquor at the exit side should be maintained at a temperature in excess of the melting point of the metal. The depth of the liquor is not a critical factor and 12 inches has been found to be satisfactory. Squeezing rollers may be used to limit the amount of liquor carried away from the floating layer at the exit side by the textile material.

Another feature of the new processes which has been found to provide for very excellent results, is the preheating of the cloth prior to contact with the floating inlet liquor. This has been discovered to provide, for example, excellent uniformity of coloration in dyeing with the new processes.

The exact temperature at which the cloth is preheated before being passed into the aqueous liquor bath is not critical. The upper limit is generally determined by the cloth itself and the temperature at which it may be safely heated without deterioration. For ordinary purposes, 120° C. can be regarded as a practical upper limit. In the preferred embodiments, the cloth is heated to between 80 and 100° C. The desired condition is to have the cloth preheated to such a temperature that upon entry into the aqueous treating liquor its temperature is such that the combination of specific heats of the cloth and of the aqueous treating liquor and any thermal effect arising from their mixing, will cause the cloth and the aqueous liquor with which it is impregnated to have a temperature not less than about 75° C. A specific example of temperature values and specific heats has been given in the previous discussion.

As has been indicated before, it has been discovered that the presence of substantial amounts of moisture in the textile material is essential during passage through the molten metal bath if the cloth is to emerge properly treated. Of course, the percentage of aqueous treating liquor present in the cloth during passage through the molten metal may be varied and will depend to a certain extent upon the particular treating solution and upon the nature of the textile material. However, as a general rule and in those cases where the metal temperature is 100° C. or below, at least about 80 percent by weight of moisture is necessary in the textile material for satisfactory results. In those cases where the metal temperature may be maintained at over 100° C., less moisture can be tolerated as a minimum owing to the ebullition that takes place as the textile material passes through the upper region of the molten metal bath or the exit thereof and the consequent resistance to metal absorption. Satisfactory results have been obtained with 60% of moisture by weight under these conditions. However, when operating at temperatures above 100° C., care must be taken to insure that there is insufficient ebullition of moisture vapor as to result in the cloth leaving the molten metal bath without any or with only a very low quantity of moisture therein, e. g., about 40% or less. The upper

limit of moisture content is not critical and in practice is primarily governed by the squeezing action of the molten metal bath. It may be as high as 200% with certain textile materials.

One of the very important features of the present invention is the very high rate of dye transferred which enables textile material to be processed at very high rates of speed. The exact speed that the textile material is passed through the treating liquor and metal baths will depend both upon the nature of the textile material, as well as the composition and nature of the aqueous treating liquor. In the case of dyeing operations, the speed will vary slightly with different dyes and also with different depths of desired shade, although in all cases the difference in speed will only amount to a few seconds. There is actually no critical lower limit on speed of textile passage and it could be actually only a fraction of a foot a minute. However, in commercial operations, it is desirable to run as rapidly as possible, and it has been found that with these new procedures, a maximum speed of 120 yards per minute or over can be obtained. Actually this upper limit has been found to be fixed by mechanical aspects of the process, and perfectly satisfactory dyeings have been obtained even at these maximum speeds.

Such speeds show how rapidly dye transfer and fixation are completed by these new procedures. As an example, if the passage through the molten metal is 10 feet and through the dye bath is 8 inches, a speed of 30 yards per minute gives an immersion of 0.44 second in the dye bath and 6.6 seconds in the molten metal. At 120 yards per minute, the cloth remains 0.11 second in the dye bath and 1.67 seconds in the metal. These short times, however, are sufficient for the dyeing to be completed and this, of course, constitutes one of the unusual and unpredictable aspects of the new procedures. In actual practice, variation of cloth speed has been found to have little or no effect on either the depth of shade or quality of dyeing, providing the time is sufficient within the baths to give the required fixation. If cloth is run at 100 yards per minute with complete fixation, slowing down to 30 yards per minute or varying the speed as often as desired, has substantially no effect on the shade. Those skilled in the art will, therefore, recognize the commercial importance of this, since it enables substantially unskilled workers to operate the equipment and still obtain satisfactory results.

As will be realized, if depth of shade or the like is desired to be varied, this will be accomplished by changing the composition of the dye bath or aqueous treating liquor.

As mentioned before, one big problem which has always confronted the dyeing industry has been the ability to transfer tests or experimental runs from the small scale over to a commercial scale. This problem does not exist with these new procedures and this constitutes a tremendous advantage therefor. Thus, by using a small scale model of the new apparatus of this invention, test runs can be made and the data obtained therefrom can be carried over without any substantial change to the commercial operations to obtain identical results in dyeing and quality.

One final feature of the new procedures is the ease with which the apparatus may be switched from one treating or dye liquor to another. Thus, at the end of any particular dyeing, all that needs to be done is to pump out the dye liquor remaining in the system, remove the exit treating liquor and circulate a cleaning solution through the system. A suitable cleaning solution is a hot solution of caustic and hydro-sulphite. After this cleaning liquor is removed, the new dye liquor and exit liquor are pumped in, and dyeing with the second shade commences immediately. In actual runs, it has been found that a complete change can be accomplished in as short a time as five minutes. This compares most favorably with the three to four hours which have been required with earlier dyeing methods and apparatus.

CONCLUSIONS

There has been presented above a general description of new processes and apparatus for modifying textile and like materials by treatment with aqueous liquors at elevated temperatures. This general description has been followed by specific examples of actual opera-

tions and also by detailed discussion of different variables associated with the procedures.

The new operations as described constitute a substantial departure from all established and known procedures for dyeing or treating of textile materials with aqueous liquors. The tremendous advantages made possible by these new type operations have already caused them to be adopted widely on a commercial scale.

We claim:

1. In the art of treating textile material in continuous length with an aqueous liquor selected from the group consisting of dyeing and dye reducing liquors and wherein the textile material is penetrable by said aqueous liquor, the steps which comprise continuously passing said textile material, without first passing the same through a bath of molten metal whereby the textile material will be free of metal penetrations and adhesions, through a fluid layer of said aqueous liquor floating on a bath of molten metal which does not chemically react with said textile material and the aqueous liquor thereon, passing the textile material directly from the aqueous liquor into said molten metal bath without exposure to the atmosphere, and continuously passing the treated textile material downwardly to a substantial depth, laterally and upwardly in a continuous molten metal path, whereby aqueous liquor taken up by the textile material as the latter travels through the floating layer may be subjected during its passage through said path of molten metal to chemical reaction, penetration and uniform squeezing due to the temperature and the pressure of the molten metal, the melting point of the metal of the molten metal bath being not more than about 100° C. and the molten metal having a temperature below that at which substantial ebullition of the aqueous liquor occurs.

2. In the process of claim 1, providing a small volume of the aqueous liquor, floating the small volume of aqueous liquor on top of the molten metal, and substantially continuously replenishing the aqueous liquor as it is absorbed by the textile material.

3. A process as recited in claim 1 in which the continuous molten metal path is longer than the path of travel of the said textile material through the said floating liquor.

4. In the art of dyeing textile material in continuous length with an aqueous dye liquor and wherein the textile material is penetrable by said aqueous liquor, the steps which comprise continuously passing said textile material, without first passing the same through a bath of molten metal whereby the textile material will be free of metal penetrations and adhesions, through a fluid layer of said aqueous liquor floating on a bath of molten metal which does not chemically react with said textile material and the aqueous dye thereon, passing the textile material directly from the aqueous liquor into said molten metal bath without exposure to the atmosphere, and continuously passing the treated textile material downwardly to a substantial depth, laterally and upwardly in a continuous molten metal path, whereby aqueous liquor taken up by the textile material as the latter travels through the floating layer may be subjected during its passage through said bath of molten metal to chemical reaction, penetration and uniform squeezing due to the temperature and the pressure of the molten metal, the melting point of the metal of the molten metal bath being not more than about 100° C. and the molten metal having a temperature below that at which substantial ebullition of the aqueous liquor occurs.

5. In the process of claim 4, floating a plurality of different aqueous dye liquors at separate locations on the surface of the molten metal, and passing separate yarns simultaneously through such separate locations, whereby the yarns are differently dyed simultaneously.

6. A process as recited in claim 4 in which the dye is selected from the group consisting of vat dyes and sulfur dyes.

7. In the art of dyeing textile material in continuous length with an aqueous dye liquor and wherein the textile material is penetrable by said aqueous liquor, the steps which comprise continuously passing said textile material, without first passing the same through a bath of molten metal whereby the textile material will be free of metal penetrations and adhesions, through a fluid layer of said aqueous liquor floating on a bath of molten metal which does not chemically react with said textile

material and the aqueous dye thereon, passing the textile material directly from the aqueous liquor into said molten metal bath without exposure to the atmosphere, and continuously passing the treated textile material downwardly to a substantial depth and upwardly in a continuous molten metal path which is substantially vertical along the greater part of its length, whereby aqueous liquor taken up by the textile material as the latter travels through the floating layer may be subjected during its passage through said bath of molten metal to chemical reaction, penetration and uniform squeezing due to the temperature and the pressure of the molten metal, the melting point of the metal of the molten metal bath being not more than about 100° C. and the molten metal having a temperature below that at which substantial ebullition of the aqueous liquor occurs.

8. In the art of dyeing textile material in continuous length with an aqueous dye liquor, said textile material having interstitial voids therein whereby the textile material is penetrable by the said aqueous liquor, the steps which comprise continuously passing said textile material, without first passing the same through a bath of molten metal whereby the textile material will be free of metal penetrations and adhesions, through a fluid layer of said aqueous liquor floating on a bath of molten metal which does not chemically react with said textile material and the aqueous dye thereon, passing the textile material directly from the aqueous liquor into said molten metal bath without exposure to the atmosphere, and continuously passing the treated textile material downwardly to a substantial depth, laterally and upwardly in a continuous molten metal path, whereby aqueous liquor taken up by the textile material as the latter travels through the floating layer may be subjected during its passage through said path of molten metal to chemical reaction, penetration and uniform squeezing due to the temperature and the pressure of the molten metal, the melting point of the metal of the molten metal bath being not more than about 100° C. and the molten metal having a temperature below that at which substantial ebullition of the aqueous liquor occurs.

9. In the art of dyeing textile material in continuous length upon which a dyestuff in unreduced form has been padded, said textile material having interstitial voids therein whereby the textile material is penetrable by an aqueous dye reducing liquor, the steps which comprise continuously passing said textile material, without first passing the same through a bath of molten metal whereby the textile material will be free of metal penetrations and adhesions, through a fluid layer of an aqueous dye reducing liquor floating on a bath of molten metal which does not chemically react with said textile material and the aqueous liquor thereon, passing the textile material directly from the aqueous liquor into the said molten metal bath without exposure to the atmosphere, and continuously passing the treated textile material downwardly to a substantial depth, laterally and upwardly in a continuous molten metal path, whereby aqueous liquor taken up by the textile material as the latter travels through the floating layer may be subjected during its passage through said path of molten metal to chemical reaction, penetration and uniform squeezing due to the temperature and the pressure of the molten metal, the melting point of the metal of the molten metal bath being not more than about 100° C. and the molten metal having a temperature below that at which substantial ebullition of the aqueous liquor occurs.

10. In the art of dyeing textile material in continuous length with an aqueous liquor containing at least one dye selected from the group consisting of vat and sulfur dyes and mixtures thereof, alkali and reducing agent, said textile material having interstitial voids therein whereby the textile material is penetrable by the said aqueous liquor, the steps which comprise continuously passing said textile material, without first passing the same through a bath of molten metal whereby the textile material will be free of metal penetrations and adhesions, through a layer of said aqueous liquor floating on a bath of molten metal which does not chemically react with said textile material and the aqueous liquor thereon, passing the textile material directly from the aqueous liquor into said molten metal bath without exposure to the atmosphere, and continuously passing the treated

textile material downwardly to a substantial depth, laterally and upwardly in a continuous molten metal path, whereby aqueous liquor taken up by the textile material as the latter travels through the floating layer may be subjected during its passage through said path of molten metal to chemical reaction, penetration and uniform squeezing due to the temperature and the pressure of the molten metal, the melting point of the metal of the molten metal bath being not more than about 100° C. and the molten metal having a temperature above 60° C. and below that at which substantial ebullition of the aqueous liquor occurs.

11. In the process of claim 10, providing a small volume of the aqueous liquor, floating the small volume of liquor on top of the molten metal, and substantially continuously replenishing the aqueous liquor as it is absorbed by the textile material.

12. In the art of dyeing textile material in continuous length upon which has been padded at least one dye selected from the group consisting of vat and sulfur dyes and mixtures thereof, said textile material having interstitial voids therein whereby the textile material is penetrable by an aqueous liquor, developing said dye by the steps which comprise continuously passing said textile material, without first passing the same through a bath of molten metal whereby the textile material will be free of metal penetrations and adhesions, through an aqueous layer of liquor containing alkali and reducing agent floating on a bath of molten metal which does not chemically react with said textile material and the aqueous liquor thereon, passing the textile material directly from the aqueous liquor into said molten metal bath without exposure to the atmosphere, and continuously passing the treated textile material downwardly to a substantial depth and upwardly in a continuous molten metal path, whereby the said aqueous liquor taken up by the textile material as the latter travels through the floating layer may be subjected during its passage through said path of molten metal to chemical reaction, penetration and uniform squeezing due to the temperature and the pressure of the molten metal, the melting point of the metal of the molten metal bath being not more than about 100° C. and the molten metal having a temperature above 60° C. and below that at which substantial ebullition of the aqueous liquor occurs.

13. In the process of claim 12, providing a small volume of the aqueous liquor, floating the small volume of liquor on top of the molten metal, and substantially continuously replenishing the aqueous liquor as it is absorbed by the textile material.

14. In the art of treating textile material in continuous length with an aqueous liquor selected from the group consisting of dyeing and dye reducing liquors and wherein the textile material is penetrable by said aqueous liquor, the steps which comprise continuously passing said textile material, without first passing the same through a bath of molten metal whereby the textile material will be free of metal penetrations and adhesions, through a fluid layer of said aqueous liquor floating on a bath of molten metal which does not chemically react with said textile material and the aqueous liquor thereon, feeding the aqueous liquor to said floating layer, preheating said aqueous liquor as it is fed to the layer whereby said aqueous liquor is introduced to said floating layer at elevated temperature, passing the textile material directly from the aqueous liquor into said molten metal bath without exposure to the atmosphere, and continuously passing the treated textile material downwardly to a substantial depth, laterally and upwardly in a continuous molten metal path, whereby aqueous liquor taken up by the textile material as the latter travels through the floating layer may be subjected during its passage through said path of molten metal to chemical reaction, penetration and uniform squeezing due to the temperature and the pressure of the molten metal, the melting point of the metal of the molten metal bath being not more than about 100° C. and the molten metal having a temperature below that at which substantial ebullition of the aqueous liquor occurs.

15. A process as recited in claim 14 in which the aqueous liquor is supplied to the said floating aqueous layer at substantially the same rate at which the aqueous liquor is taken up by the material passing therethrough whereby said aqueous layer may be maintained at rela-

tively small constant volume and at substantially constant temperature and strength.

16. A process as recited in claim 15 in which the aqueous liquor employed to replenish the aqueous liquor in the said layer is heated from a temperature of about 25° to 30° C. to about 80° C. just prior to its addition to the layer.

17. A process as recited in claim 15 in which a portion of the said aqueous liquor floating on the molten metal bath is withdrawn, heated to a temperature of about 80° C., and then recycled for return to the body of liquor from which it was withdrawn at a sufficient rate to maintain the temperature of the floating liquor substantially constant.

18. A process as recited in claim 14 in which the said aqueous liquor contains hydrosulphite.

19. In the art of treating textile material in continuous length with an aqueous liquor selected from the group consisting of dyeing and dye reducing liquors and wherein the textile material is penetrable by said aqueous liquor, the steps which comprise continuously preheating said textile material and continuously passing said heated textile material, without first passing the same through a bath of molten metal whereby the textile material will be free of metal penetrations and adhesions, through a fluid layer of said aqueous liquor floating on a bath of molten metal which does not chemically react with said textile material and the aqueous liquor thereon, passing the textile material directly from the aqueous liquor into said molten metal bath without exposure to the atmosphere, and continuously passing the treated textile material downwardly to a substantial depth, laterally and upwardly in a continuous molten metal path, whereby aqueous liquor taken up by the textile material as the latter travels through the floating layer may be subjected during its passage through said path of molten metal to chemical reaction, penetration and uniform squeezing due to the temperature and the pressure of the molten metal, the melting point of the metal of the molten metal bath being not more than about 100° C. and the molten metal having a temperature below that at which substantial ebullition of the aqueous liquor occurs.

20. In the art of treating textile material in continuous length with an aqueous liquor selected from the group consisting of dyeing and dye reducing liquors and wherein the textile material is penetrable by said aqueous liquor, the steps which comprise continuously heating said textile material to a temperature between 70° C. and 120° C. and continuously passing said heated textile material, without first passing the same through a bath of molten metal whereby the textile material will be free of metal penetrations and adhesions, through a fluid layer of said aqueous liquor floating on a bath of molten metal which does not chemically react with said textile material and the aqueous liquor thereon, passing the textile material directly from the aqueous liquor into said molten metal bath without exposure to the atmosphere, and continuously passing the treated textile material downwardly to a substantial depth, laterally and upwardly in a continuous molten metal path, whereby aqueous liquor taken up by the textile material as the latter travels through the floating layer may be subjected during its passage through said path of molten metal to chemical reaction, penetration and uniform squeezing due to the temperature and the pressure of the molten metal, the melting point of the metal of the molten metal bath being between about 60° C. and about 100° C., said molten metal having a temperature above 60° C. and below that at which substantial ebullition of the aqueous liquor occurs.

21. A process as recited in claim 20 in which said floating aqueous layer contains hydrosulphite together with an antioxidant to inhibit the formation of sludge on the surface of the molten metal bath.

22. A process as recited in claim 20 in which said floating aqueous layer is maintained in comparatively small volume and is substantially continuously replenished with fresh aqueous liquor as the same is absorbed by said textile material, said replenishing liquor being heated to approximately the temperature of said floating aqueous layer as it is supplied to said layer.

23. A process as recited in claim 20 in which the temperature of the preheated impregnated textile material is above the freezing point of the metal in the molten metal bath when it enters said bath.

24. In the art of treating textile material in continuous

length with an aqueous liquor selected from the group consisting of dyeing and dye reducing liquors and wherein the textile material is penetrable by said aqueous liquor, the steps which comprise continuously passing said textile material, without first passing the same through a bath of molten metal whereby the textile material will be free of metal penetrations and adhesions, through a fluid layer of said aqueous liquor floating on a bath of molten metal which does not chemically react with said textile material and the aqueous liquor thereon, passing the textile material directly from the aqueous liquor into said molten metal bath without exposure to the atmosphere, and continuously passing the treated textile material downwardly to a substantial depth, laterally and upwardly in a continuous molten metal path, whereby aqueous liquor taken up by the textile material as the latter travels through the floating layer may be subjected during its passage through said path of molten metal to chemical reaction, penetration and uniform squeezing due to the temperature and the pressure of the molten metal, the melting point of the metal of the molten metal bath being not more than about 100° C. and the molten metal having a temperature below that at which substantial ebullition of the aqueous liquor occurs, and then passing said textile material through an aqueous liquor, which is inert to the molten metal and is not deleterious to the dyeing liquor on the textile material, floating on the surface of said molten metal bath at the exit side of said molten metal bath where said textile material leaves said bath to thereby reduce the tendency of said textile material to pick up scum and particles of molten metal.

25. The art of treating textile material in continuous length as recited in claim 24 in which said aqueous liquor floating at the exit side of said metal bath is a solution of a salt selected from the group consisting of sodium chloride and Glauber salt.

26. The art of treating textile material in continuous length as recited in claim 25 in which said aqueous treating liquor contains hydrosulphite and said aqueous liquor floating at the exit side of said metal bath is maintained alkaline.

27. The art of treating textile material in continuous length as recited in claim 24 in which said aqueous liquor floating at the exit side of said metal bath is a solution of a lower saturated mono-carboxylic acid.

28. In the art of treating textile material in continuous length with an aqueous hydrosulphite containing liquor selected from the group consisting of dyeing and dye reducing liquors and wherein the textile material is penetrable by said aqueous liquor, the steps which comprise continuously passing said textile material, without first passing the same through a bath of molten metal whereby the textile material will be free of metal penetrations and adhesions, through a fluid layer of said aqueous liquor floating on a bath of molten metal which does not chemically react with said textile material and the aqueous liquor thereon, passing the textile material directly from the aqueous liquor into said molten metal bath without exposure to the atmosphere, and continuously passing the treated textile material downwardly to a substantial depth, laterally and upwardly in a continuous molten metal path, whereby aqueous liquor taken up by the textile material as the latter travels through the floating layer may be subjected during its passage through said path of molten metal to chemical reaction, penetration and uniform squeezing due to the temperature and the pressure of the molten metal, the melting point of the metal of the molten metal bath being not more than about 100° C. and the molten metal having a temperature below that at which substantial ebullition of the aqueous liquor occurs, said aqueous hydrosulphite containing liquor also containing an amount of an antioxidant effective to inhibit the tendency of said hydrosulphite to decompose to form products which attack the metal of the molten metal bath to form a sludge on the surface of the molten metal bath.

29. A process as recited in claim 28 in which said antioxidant is a reducing sugar.

30. Apparatus for the continuous treatment of textile material in continuous length comprising a vessel having side and end walls and a bottom, a vertical partition member in the vessel between the side walls and spaced from the bottom, the inner faces of the side and end walls and the faces of the partition member together

defining a passage of U-shape whose limbs are substantially wholly vertical and through which the material passes, the inner faces of the side walls being closely spaced along their length from the faces of the partition member, said faces presenting narrow projections to prevent sticking of the said material thereto, said passage forming a container for molten metal and having a substantially vertical downward entry run and a substantially vertical upward exit run, and an open-bottomed trough at the top of the entry run for supporting a layer of treating liquor on the surface of the molten metal so that the material passes through the treating liquor prior to entering the molten metal, and heating means thermally connected with said side walls and said vertical partition member for maintaining the metal which is to be placed within the said container in molten condition.

31. An apparatus as recited in claim 30 in which the said heating means are disposed within said side walls and said vertical partition member.

32. An apparatus as recited in claim 30 in which there is provided means for automatically maintaining the treating liquor at a substantially constant depth in the trough.

33. An apparatus as recited in claim 30 in which molten metal having a melting point not more than about 100° C. fills said U-shaped passage and extends above the bottom of said trough.

34. An apparatus as recited in claim 30 in which metal having a melting point not more than about 100° C. fills said U-shaped passage and extends above the bottom of said trough.

35. In the art of treating textile material in continuous length with an aqueous liquor selected from the group consisting of dyeing and dye reducing liquors and wherein the textile material is penetrable by said aqueous liquor, the steps which comprise continuously heating said textile material to a temperature between 70° C. and 120° C. and continuously passing said heated textile material, without first passing the same through a bath of molten metal whereby the textile material will be free of metal penetrations and adhesions, through a fluid layer of said aqueous liquor floating on a bath of molten metal which does not chemically react with said textile material and the aqueous liquor thereon, said floating aqueous layer being maintained in comparatively small volume and being substantially continuously replenished with fresh aqueous liquor as the same is absorbed by said textile material, said replenishing liquor being heated to approximately the temperature of said floating aqueous layer as it is supplied to said layer, passing the textile material directly from the aqueous liquor into said molten metal bath without exposure to the atmosphere, and continuously passing the treated textile material downwardly to a substantial depth, laterally and upwardly in a continuous molten metal path, whereby aqueous liquor taken up by the textile material as the latter travels through the floating layer may be subjected during its passage through said path of molten metal to chemical reaction, penetration and uniform squeezing due to the temperature and the pressure of the molten metal, the melting point of the metal of the molten metal bath being between about 60° C. and about 100° C., said molten metal having a temperature about 60° C. and below that at which substantial ebullition of the aqueous liquor occurs, and then passing said textile material through an aqueous liquor, which is inert to the molten metal and is not deleterious to the dyeing liquor on the textile material, floating on the surface of said molten metal bath where said textile material leaves said bath to thereby reduce the tendency of said textile material to pick up scum and particles of molten metal.

36. In the art of treating textile material in continuous length with an aqueous hydrosulphite containing liquor selected from the group consisting of dyeing and dye reducing liquors and wherein the textile material is penetrable by said aqueous liquor, the steps which comprise continuously passing said textile material, without first passing the same through a bath of molten metal whereby the textile material will be free of metal penetrations and adhesions, through a fluid layer of said aqueous liquor floating on a bath of molten metal which does not chemically react with said textile material and the aqueous liquor thereon, said floating aqueous layer being maintained in comparatively small volume and being substantially continuously replenished with fresh aqueous liquor as the same is absorbed by said textile material, said replenishing liquor being heated to approximately the temperature of said floating aqueous layer as it is supplied to said layer, passing the textile material directly from the aqueous liquor into said molten metal bath without exposure to the atmosphere, and continuously passing the treated textile material downwardly to a substantial depth, laterally and upwardly in a continuous molten metal path, whereby aqueous liquor taken up by the textile material as the latter travels through the floating layer may be subjected during its passage through said path of molten metal to chemical reaction, penetration and uniform squeezing due to the temperature and the pressure of the molten metal, the melting point of the metal of the molten metal bath being not more than about 100° C. and the molten metal having a temperature below that at which substantial ebullition of the aqueous liquor occurs, said aqueous hydrosulphite containing liquor also containing an amount of an antioxidant effective to inhibit the tendency of said hydrosulphite to decompose to form products which attack the metal of the molten metal bath to form a sludge on the surface of the molten metal bath, and then passing said textile material through an aqueous liquor, which is inert to the molten metal and is not deleterious to the dyeing liquor on the textile material, floating on the surface of said molten metal bath at the exit side of said molten metal bath where said textile material leaves said bath to thereby reduce the tendency of said textile material to pick up scum and particles of molten metal.

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